

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
5 January 2006 (05.01.2006)

PCT

(10) International Publication Number
WO 2006/001530 A2

- (51) International Patent Classification: Not classified
(21) International Application Number: PCT/JP2005/012266
(22) International Filing Date: 27 June 2005 (27.06.2005)
(25) Filing Language: English
(26) Publication Language: English
(30) Priority Data: 2004-190482 28 June 2004 (28.06.2004) JP
(71) Applicant (for all designated States except US): CANON KABUSHIKI KAISHA [JP/JP]; 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP).
(72) Inventors; and
(75) Inventors/Applicants (for US only): KUBOTA, Masahiko [JP/JP]; c/o CANON KABUSHIKI KAISHA, 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP). SUZUKI, Takumi [JP/JP]; c/o CANON KABUSHIKI KAISHA, 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP). SATO, Tamaki [JP/JP]; c/o CANON KABUSHIKI KAISHA, 3-30-2, Shimomaruko, Ohta-ku,

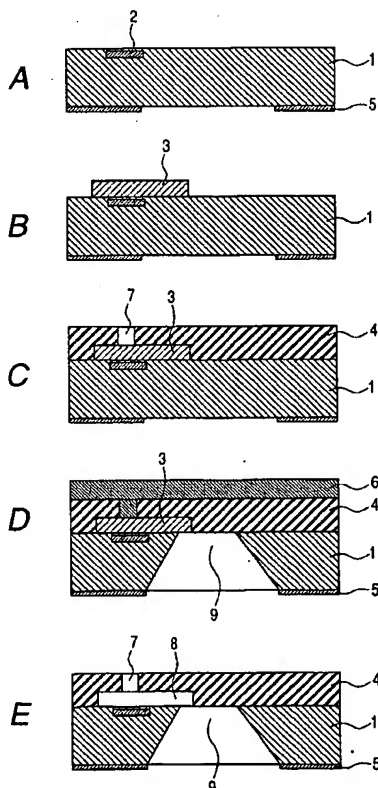
Tokyo 1468501 (JP). KANRI, Ryoji [JP/JP]; c/o CANON KABUSHIKI KAISHA, 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP). HATTA, Maki [JP/JP]; c/o CANON KABUSHIKI KAISHA, 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP). ASAI, Kazuhiro [JP/JP]; c/o CANON KABUSHIKI KAISHA, 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP). SHIBA, Shoji [JP/JP]; c/o CANON KABUSHIKI KAISHA, 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP). HINO, Etsuko [JP/JP]; c/o CANON KABUSHIKI KAISHA, 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP). ISHIKURA, Hiroe [JP/JP]; c/o CANON KABUSHIKI KAISHA, 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP). OKANO, Akihiko [JP/JP]; c/o CANON KABUSHIKI KAISHA, 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP).

(74) Agents: OKABE, Masao et al.; No. 602, Fuji Bldg., 2-3, Marunouchi 3-chome, Chiyoda-ku, Tokyo 1000005 (JP).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,

[Continued on next page]

(54) Title: LIQUID DISCHARGE HEAD MANUFACTURING METHOD, AND LIQUID DISCHARGE HEAD OBTAINED USING THIS METHOD



(57) Abstract: According to the present invention, a method for manufacturing a liquid discharge head includes the steps of depositing a solid layer for forming a flow path on a substrate on which an energy generating element is arranged to generate energy that is used to discharge liquid, forming, on the substrate where the solid layer is mounted, a coating layer for coating the solid layer, forming a discharge port used to discharge a liquid, through a photolithographic process, in the coating layer formed on the solid layer, and removing the solid layer to form a flow path that communicates with the energy element and the discharge port, whereby a material used for the coating layer contains a cationically polymerizable chemical compound, cationic photopolymerization initiator and an inhibitor of cationic photopolymerization, and whereby a material of the solid layer that forms a boundary with a portion where the discharge port of the coating layer is formed contains a copolymer of methacrylic anhydride and methacrylate ester.

BEST AVAILABLE COPY



CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

DESCRIPTION

LIQUID DISCHARGE HEAD MANUFACTURING METHOD, AND
LIQUID DISCHARGE HEAD OBTAINED USING THIS METHOD

5

Technical Field

The present invention relates to a liquid discharge head manufacturing method, and a liquid discharge head obtained using this manufacturing method. Specifically, the present invention relates to a method for manufacturing a liquid discharge (ejection) recording head that ejects a liquid and performs recording, and a liquid discharge (ejection) recording head obtained using this manufacturing method.

15

Background Art

Generally, liquid ejection recording heads (including ink jet recording heads and ink jet heads) employing a liquid ejection recording system (including an ink jet recording system) comprise a plurality of tiny discharge ports, a plurality of flow paths and a plurality of liquid discharge means provided along part of these flow paths. In order to eject ink from the liquid ejection recording head onto recording paper to obtain high quality images, it is preferable that the same volume of ink be

25

discharged at the same discharge speed from the individual discharge ports. Further, the shape of the boundary face between each discharge port and the corresponding communication flow path must not
5 adversely affect the discharge of ink.

As a method for manufacturing an ink jet recording head, a method is described in Japanese Patent Application Laid-Open No. H06-286149, according to which an ink flow path pattern is formed
10 by using a dissolvable resin, and is coated by an epoxy resin, and according to which, thereafter, discharge ports are formed and the dissolvable resin is removed. Further, another method is disclosed in Japanese Patent Laid-Open Application No. 2001-179990,
15 according to which a substance that inhibits photo curing of a discharge port formation material is mixed with a removable resin.

For the discharge of extremely small droplets, a liquid flow resistance at the discharge port of the
20 liquid ejection recording head must be reduced, and the liquid ejection speed must be maintained. In Japanese Patent Laid-Open Application No. 2003-25595, an idea is disclosed according to which two layers of dissolvable resin are formed, and an intermediate
25 portion (an intermediate chamber), narrower than substrate flow paths and wider than distal ends of the discharge ports, is provided between the

substrate flow paths and the distal ends of the discharge ports.

Recently, as the image quality of ink jet (IJ) printers has become highly competitive, the size of ink droplets to be discharged has been reduced. And as the size of ink droplets has been reduced, the diameter of the orifice (the diameter of the discharge port, of the IJ head) that discharges ink droplets has also become smaller. However, in the cross section of a conventional IJ head shown in FIG. 13A, when the diameter of a discharge port 909 is reduced without its thickness PH (OP thickness) being changed, the flow resistance of ink at the discharge port 909 is increased in proportion to the square of the diameter of the discharge port 909. As a result, when the discharge of ink is started, following a pause, e.g., after the printer has been halted, the characteristic of the discharge of ink droplets tends to be deteriorated at the first discharge (this phenomenon is called an "incomplete discharge phenomenon"). It should be noted that in FIGS. 13A to 13C the other components are a substrate 901, a heat generating resistor 902 and a flow path formation member 907 and that MH denotes a flow path height.

In order to stably launch small droplets, the present inventors attempted to manufacture a small

droplet nozzle wherein, as shown in FIGS. 13B and 13C, the diameter of a discharge port was small and the OP thickness (PH) was reduced (e.g., about $PH \leq 10 \mu m$). When this ink jet recording head was manufactured, however, using the methods described in the above-described patent publications, new technical problems were found.

Specifically, as one phenomenon, a scum occurs at the interface between a removable resin and a discharge port formation material used for forming ink discharge ports, and the direction in which ink droplets are ejected from the discharge port faces is bent, so that a printed image is deteriorated. This phenomenon could not be resolved using the method disclosed in Japanese Patent Laid-Open Application No. 2001-179990.

The present inventors thoroughly studied this phenomenon and arrived at the following conclusion. The discharge port formation material is a negative type resist, and the discharge ports are formed during the photolithography process. That is, since the negative type resist is employed to form a cured layer, including discharge ports, UV light irradiation is performed through a mask (not shown) for an area other than the discharge ports. At this time, the amount of light irradiating a unit area is larger in an area wherein the removable resin is

present than in an area wherein the resin is not present. When the diameter of a discharge port is small, during light irradiation, the amount of light (per unit area) that reaches an unexposed portion (a discharge port area) is increased.

As a result, for a shape wherein the flow path height is extended and the PH (OP thickness) is thin, the difference in the amount of irradiated light is increased even more. Through an analysis of the cross section of the minute discharge port, it was found the scum can be clearly observed at the interface between the removable resin and the discharge port formation material used for forming ink discharge ports.

Based on the above new view, the present inventors realized that there was a problem with the complete removal of a scum that occurs at the interface between a removable resin and a discharge port formation material, used for forming ink discharge ports having the nozzle shape of an IJ head, as shown in FIGS. 13B and 13C, whereat the difference in the amount of irradiated light is increased.

Disclosure of the Invention

While taking the above shortcoming into account, the objective of the present invention is to provide a method for manufacturing a liquid discharge head

whereby a dissolvable and removable solid layer,
which is a mold for defining a flow path pattern, and
a discharge port formation material layer, which
coats the solid layer, are employed, and whereby a
5 scum does not occur at the interface whereat these
layers make direct contact, and small droplets
(including extremely small droplets) are accurately
discharged at the discharge ports and a liquid
ejection head obtained using this manufacturing
10 method.

To achieve this objective, according to the
invention, a method for manufacturing a liquid
discharge head comprises the steps of:

forming a solid layer, for forming a flow path,
15 on a substrate on which an energy generating element
is arranged to generate energy that is used to
discharge liquid;

forming, on the substrate whereon the solid
layer is mounted, a coating layer for coating the
20 solid layer;

forming a discharge port used to discharge a
liquid, through a photolithography process, in the
coating layer deposited on the solid layer; and

removing the solid layer to form a flow path
25 that communicate with the energy element and the
discharge port,

whereby a material used for the coating layer

contains a cationically polymerizable chemical compound, a cationic photopolymerization initiator and an inhibitor of cationic photopolymerization, and whereby a material used for the solid layer

5. that forms a boundary, with a portion wherein the discharge port of the coating layer are formed, contains a copolymer of methacrylic anhydride and methacrylate ester.

A liquid discharge head according to this invention is manufactured using the above described manufacturing method, and a discharge port formation material for forming a discharge port for this head contains a cationically polymerizable chemical compound, a cationic photopolymerization initiator and an inhibitor of cationic photopolymerization.

Brief Description of the Drawings

FIGS. 1A, 1B, 1C, 1D and 1E are diagrams showing the processing for forming ink flow paths according to a first embodiment of the present invention;

FIG. 2 is a diagram showing an absorption spectrum for P(PMMA-MAA) used for the invention;

FIG. 3 is a diagram showing an absorption spectrum for resin composite 1, which is used for the invention;

FIGS. 4A, 4B, 4C, 4D, 4E and 4F are diagrams

for explaining example processing for forming a solid layer applicable for the present invention;

FIGS. 5A, 5B, 5C, 5D, 5E, 5F, 5G and 5H are diagrams showing the processing for forming ink flow paths according to a second embodiment of the present invention;

FIGS. 6A, 6B, 6C, 6D, 6E, 6F and 6G are diagrams showing the processing for forming ink flow paths according to a third embodiment of the present invention;

FIG. 7 is a diagram for explaining a correlation between the wavelength of an exposure apparatus and the illuminance thereof used for a liquid discharge head manufacturing method according to the present invention;

FIG. 8 is an explanatory diagram showing an ink jet head unit manufactured using the liquid discharge head manufacturing method of the present invention;

FIGS. 9A, 9B, 9C, 9D, 9E, 9F, 9G, 9H and 9I are diagrams showing the processing for forming ink flow paths according to a fourth embodiment of the present invention;

FIG. 10 is an explanatory cross-sectional view of an ink jet head according to a fifth embodiment of the present invention;

FIG. 11 is an explanatory cross-sectional view of an ink jet head according to a sixth embodiment of

the present invention;

FIG. 12 is an explanatory cross-sectional view of an ink jet head according to a seventh embodiment of the present invention;

5 FIGS. 13A, 13B and 13C are schematic cross-sectional views of a conventional nozzle shape for discharging small droplets; and

FIGS. 14A and 14B are diagrams for specifically explaining a scum occurrence state.

10

Best Mode for Carrying Out the Invention

The present invention will now be described by employing, as an example liquid discharge head, an ink jet head (IJ head) that performs recording using
15 ink. However, the liquid discharge head for this invention may be a type that can also employ various kinds of liquids, for a variety of surfaces, for purposes other than recording. In the specifications for this invention, ionizing radiation is a general
20 term for radiation, such as by Deep-UV light, electrons or X rays, that affects the ionization of a material.

(Explanation of a scum production mechanism)

First, an explanation will be given for a new
25 view by the present inventors concerning a mechanism wherein a scum occurs at the interface between a solid layer, which is formed by using a removable

resin, and a coating layer, which is formed by using a discharge port formation material for forming ink discharge ports. The present inventors have assumed that, for the mechanism, two factors cause scum to occur (see FIGS. 14A and 14B). In FIGS. 14A and 14B, reference numeral 801 denotes a substrate; 802, a heat generation resistor; 807, an ink flow path formation member; and 809, a discharge port. Scum 820 occurs in a lower portion 809a of the discharge port 809.

(1): When light is projected onto the coating layer, which is formed by using a photo curing composite that is a cationically polymerizable, nozzle formation material, the light spreads along the interface between the solid layer and the coating layer into the area, blocked by a mask, in which discharge ports are to be formed, and as a result, a tiny cured portion is generated.

(2): At the interface between the solid layer and the coating layer for forming an ink discharge port, a compatible layer is formed of the materials used for these layers, and the presence of this layer causes scum to occur.

These two factors do not individually contribute to the occurrence of the scum, but when combined, may be related to the occurrence of the scum. Thus, it is the understanding of the present

inventors that, to eliminate the scum, it is important that the problems posed by the two factors be resolved at the same time.

The present inventors carefully studied the
5 nozzle shape of an IJ head whereat there was no scum, and took the following measures to resolve the problems posed by the above described assumed factors.

Measure 1: A inhibitor of cationic
photopolymerization was added to a discharge port
10 formation material that contains a cationic photopolymerizable chemical compound and a cationic photopolymerization initiator. With the inhibitor of cationic photopolymerization, upon the irradiation with light, a photopolymerizable reaction was
15 adjusted at the interface between the exposed portion and the non-exposed portion, and cationic polymerizable reaction was inhibited by the light that reached the non-exposed portion.

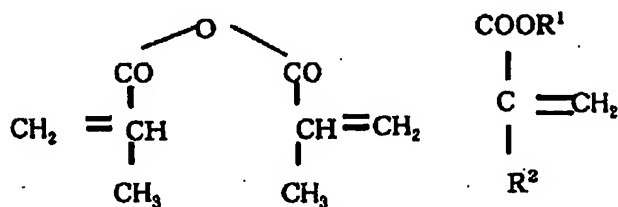
Measure 2: A copolymer of methacrylate ester
20 and methacrylic anhydride is employed as the solid layer formation resin that directly contacts the discharge port formation member to aggressively obtain the compatibility between the solid layer (removable resin layer) and the solvent contained in
25 a coating liquid that is used to form a coated layer that is made of the discharge port formation material. And the obtained compatible layer has a property that

it can be completely dissolved in a development liquid used to develop the discharge port formation material.

By applying measures 1 and 2 at the same time, when IJ nozzles of various types and having various shapes were formed, scum did not occur at the interface between the removable resin and the nozzle formation material used for forming ink discharge ports.

10 (Explanation of a photosensitive material)

In this invention, a positive type photosensitive composite, the resin element of which is a copolymer of methacrylic anhydride and methacrylate ester, is at least employed as a solid layer that is the mold for a flow path pattern. This copolymer is obtained by polymerization of methacrylic anhydride and methacrylate ester in the following chemical formula.



20 The ratio of methacrylic anhydride to the copolymer can be selected preferably from 5 to 30 mass%, or more preferably from 8 to 12 mass% relative to the total amount of methacrylic anhydride and

methacrylate ester.

R^2 in the methacrylate ester element represents an alkyl group having carbon numbers of one to three, and R^1 represents an alkyl group having carbon
5 numbers of one to three. R^1 and R^2 independently represent the above definitions, that is, at least one type of methacrylate ester expressed in the above expression can be copolymerized with methacrylic anhydride. This copolymer can be obtained from the
10 above monomer elements, and the polymerization form is not especially limited, and may be random polymerization or block polymerization so long as a desired positive type resist characteristic can be obtained. Further, as the copolymer, it is
15 preferable that the molecular weight be 20000 to 100000 (weight average) and the degree of dispersion (M_w/M_n) be 1.2 to 4.0.

It is preferable that an area of 200 to 260 nm be the only absorbed wavelength area for
20 decomposition of the resin element of this photosensitive resin composite. Further, for the development, after light irradiation, of a liquid mixture of diethylene glycol, morpholine, monoethanolamine and pure water can be employed.

25 On the other hand, for a laminated structure of multiple solid layers, e.g., two solid layers that have a stair shaped stepped portion, the upper layer

- is formed of a resin composite that contains a copolymer of methacrylic anhydride and methyl methacrylate. The lower layer is formed of a positive type resin composite, a photosensitive wavelength (an absorbed wavelength) of which differs from that of the copolymer of methacrylic anhydride and methyl methacrylate, and with which the copolymer contained in the upper layer is not decomposed while the lower layer is exposed.
- 5 Polymethylisopropenylketone, for example, is preferable as the resin element of the resin composite for the lower layer.
- 10

- A photocurable composite that contains a cationically polymerizable chemical compound, a cationic photopolymerization initiator and a inhibitor of cationic photopolymerization is employed as a curable composite of a negative photosensitive type as a discharge port formation material. The cationically polymerizable chemical compound contained in the photocurable composite is used to combine compounds by using a cationic addition polymerization reaction. For example, an epoxy compound in the solid state at normal temperature, described in Japanese Patent No. 3,143,307, can be appropriately employed. This epoxy compound can, for example, be a reactant of bisphenol A and epichlorohydrin, the molecular weight of which is, at
- 15
- 20
- 25

the least, about 900, a reactant of bromine-containing phenol A and epichlorohydrin, a reactant of phenolnovolac or ortho-cresolnovolac and epichlorohydrin, or a multi-reactive epoxy resin

5 having an oxycyclohexane framework described in Japanese Patent Laid-Open Application Nos. S60-161973, S63-221121, S64-9216 and H02-140219, and one or more of two types of these epoxy compounds can be employed. Further, for these epoxy compounds, preferably, the

10 equivalent epoxy weight is equal to or smaller than 2000, or more preferably, is equal to or smaller than 1000. This is because, when the equivalent epoxy weight exceeds 2000, the bridge density is reduced as a result of the curing reaction, and either Tg, or

15 the heat deflection temperature of the cured product, will be reduced, or the adhesiveness and the ink resistance will be deteriorated.

The cationic photopolymerization initiator can be, for example, an aromatic iodonium salt or an

20 aromatic sulfonium salt (see J. POLYMER SCI: Symposium No. 56 383-395 (1976)), or SP-150 or SP-170, marketed by Asahi Denka Kogyo Kabushiki Kaisha. When the cationic photopolymerization initiator, together with a reducing agent, is heated, the cationic

25 addition polymerization reaction can be accelerated (the bridge density can be improved, compared with when independent cationic photopolymerization is

employed). However, when the cationic photopolymerization initiator and a reducing agent are to be employed together, the reducing agent must be selected so that the resultant initiator is a so-called redox initiator that does not react at normal temperature, but reacts at a specific temperature or higher (preferably, 60°C or higher). Such a reducing agent is a copper compound, and copper triflate (trifluoromethane copper(II) sulfonate), especially, is the optimal agent, when the reactivity and the solubility of the epoxy resin are taken into account. A reducing agent, such as ascorbate, is also effective. When a higher bridge density (a high Tg) is required due to an increase in the number of nozzles (for high-speed printing) or the use of a non-neutral ink (an improvement in the waterproofing of a coloring agent); as will be described later, the above described reducing agent is employed as a solution after the coating resin layer has been developed, and the coating resin layer need only be immersed and heated at the postprocess step. In this manner, the bridge density can be increased.

An addition agent can be added, as needed, to the photocurable composite. For example, a flexibility-providing agent may be added to reduce the coefficient of the elasticity of an epoxy resin, or a silane coupling agent may be added to obtain a

greater bonding force with a substrate.

The inhibitor of cationic photopolymerization is also added to the photocurable composite. The inhibitor of cationic photopolymerization adjusts the curing of a photocurable composite to inhibit the formation of a cured layer by light that reaches the unexposed portion that is used as a discharge port, at the interface between the positive type resist layer (solid layer) and the negative type resist layer (nozzle formation material layer) that was previously described. An arbitrary inhibitor of cationic photopolymerization can be employed so long as a desired curing characteristic at the light irradiation portion and scum occurrence prevention effects are obtained, and so long as the function of an acid catalyst can be degraded. Generally, a basic material is employed as a inhibitor of cationic photopolymerization, and a compound that can be used as an acceptor for protons, i.e., a basic material having a pair of nonshared electrons is appropriate. A nitrogen-containing compound having a pair of nonshared electrons is a compound that acts as a base relative to acid and that can effectively prevent the occurrence of scum. A specific nitrogen-containing compound is a compound containing nitrogen atoms, sulfur atoms or phosphorus atoms, and a typical example is an amine compound. Specifically, such

amine compounds are: an amine, such as diethanolamine, triethanolamine or triisopropanolamine, replaced by a hydroxyalkyl having a carbon number of one or greater to four or smaller; a pyrimidine compound, such as pyrimidine, 2-aminopyrimidine or 4-aminopyrimidine; a pyridine compound, such as pyridine or methyl pyridine; and aminophenol, such as 2-aminophenol or 3-aminophenol.

The content of a basic material is preferably 0.01 to 100 weight% relative to the cationic photopolymerization initiator, and more preferably 0.1 to 20 weight%. Two or more types of basic materials may be employed together.

The negative type resist layer is exposed through a mask that blocks a portion that is to be used as a discharge port, and the portion other than the blocked portion (the non-exposed portion) is cured. Then, the negative type resist layer is developed by using a development liquid to remove the non-exposed portion, and the discharge port is formed. Any type of general-purpose exposure apparatus may be employed for this pattern exposure; however, it is preferable that an exposure apparatus irradiate light in a wavelength area that matches the absorbed wavelength area of the negative type resist layer and that does not overlap the absorbed wavelength area of the positive type resist layer. It is also

preferable that an aromatic solvent, such as xylene, be employed to develop the negative type resist layer after the pattern exposure has been performed.

The preferred embodiments of the present invention will now be described in detail while referring to the accompanying drawings.

(First Embodiment)

FIGS. 1A to 1E are schematic cross-sectional views showing the processing for a method according to a first embodiment of this invention for manufacturing a liquid discharge head. The method for manufacturing a liquid discharge head according to this embodiment will now be explained while referring to FIGS. 1A to 1E.

In FIG. 1A, heat generation devices 2, which are liquid discharge energy generating elements, transistors, which independently drive the heat generation devices, and a circuit (not shown), which processes data signals, for example, are mounted on a silicon substrate 1, and are electrically connected by wiring. A nitride film 5 is used as a mask for forming an ink supply port 9 that will be described later.

Then, as shown in FIG. 1B, a positive resist layer 3 is coated on the silicon substrate 1 as a dissolvable and removable solid layer, and baked. A general solvent coating method, such as spin coating

or bar coating, can be employed for the coating of this layer. A positive type resist composite that contains the above-described copolymer of methacrylic anhydride and methyl methacrylate as resin elements
5 is employed as a solid layer formation material. The baking temperature is 120 to 150°C, and the baking period is three to ten minutes. The thickness of the film is 10 to 20 μm .

Next, a shortwave ultraviolet (hereinafter referred to as DeepUV) irradiation apparatus (not
10 shown) is employed to irradiate the positive type resist through a mask (not shown) using light having a wavelength of 200 to 300 nm. At this time, as shown in FIG. 2, since the absorbed wavelength area
15 of the positive type resist is 200 to 260 nm, the decomposition reaction at the light irradiated portion is accelerated by the wavelength of the irradiating light (the energy distribution). Then, the positive type resist layer 3 is developed. A
20 development liquid can be a liquid mixture of diethylene glycol, morpholine, monoethanolamine and pure water. Through the development process, a predetermined mold pattern, corresponding to flow paths, can be obtained.

25 Sequentially, a negative type resist layer 4, used as a discharge port formation material, is coated to cover the positive type resist layer 3. A

common solvent coating method, such as spin coating, can be employed for this coating.

Resin composite 1 having the following composition is employed as a negative type resist composite that is a discharge port formation material (a film thickness of 10 μm on the positive type resist layer 3: see FIG. 1B). For the formation of the negative type resist composite, the resin composite 1 is dissolved in a solvent mixture of methyl isobutyl ketone and xylene at a density of 60 mass%, and the resultant composite is used for spin coating.

Resin Composite 1:

Epoxy resin (EHPE-3158 by Daicel Chemical Industries, Ltd.): 100 parts by weight
Silane coupling agent (A-187 by Nippon Unicar Co., Ltd.): 1 part by weight

Cationic photopolymerization initiator (SP-170 by Asahi Denka Kogyo K.K.): 1.5 parts by weight

Cationic photopolymerization inhibitor (triethanolamine): 13 mol% relative to SP-170

An arbitrary general exposure apparatus can be employed for this pattern exposure process. However, as shown in FIG. 3, it is preferable that an exposure apparatus irradiate light having a wavelength area that matches the absorbed wavelength area (indicated by a broken line in FIG. 3) of the negative type

resist layer (the negative type coated resin 1) and that does not match the absorbed wavelength area (200 to 250 nm in this embodiment) of the positive type resist layer 3. It is also preferable that an aromatic solvent, such as xylene, be employed for the development of the negative type resist layer 4 after the exposure pattern has been completed. The state wherein a discharge port 7, which reaches the positive type resist layer 3, is formed in the cured layer 4 of the negative type resist layer is shown in FIG. 1C.

Following this, in order to obtain a structure shown in FIG. 1D, one side of the substrate 1 is protected with a resin 6 that coats the face whereat the discharge port 7 is formed, and by anisotropic etching, an ink supply port 9 is formed from the reverse face of the silicon substrate 1 using an alkaline solution, such as TMAH (tetramethylammonium hydride). Thereafter, the resin 6 is dissolved and removed, and an ionizing radiation of 300 nm or lower is collectively projected across the cured layer 4 of the negative type resist layer. The purpose of this radiation is the decomposition of the copolymer, which consists of the positive type resist layer 3, and the reduction of the molecular weight, so that the resin 6 can be easily removed. Finally, the positive type resist layer 3, used for the mold, is

removed using a solvent, and the state shown in FIG. 1E is obtained. As a result, an ink channel, extending from the ink supply port 9, along the flow path 8, to the discharge port 7, is formed.

5 Since the above-described method employs a solvent coating method, such as spin coating, used for a semiconductor manufacturing technique, ink flow paths can be formed for which the heights are extremely accurate and stable. In addition, since
10 the photolithography technique for semiconductors is employed for the two-dimensional shape parallel to the substrate, accuracy at a sub-micron level can be attained. Furthermore, since a radical
15 polymerization inhibitor is mixed with the negative type resist composite, and since a copolymer of methacrylic anhydride and methacrylate ester is employed for the positive type resist layer, the
20 formation of a scum is prevented at the above-described interface with the negative type resist layer that is overlaid.

(Second Embodiment)

FIGS. 4A to 4F are cross-sectional views for explaining example solid layer formation processing that can be employed for the present invention. A
25 second embodiment of this invention differs from the first embodiment in that a laminated structure, for which a plurality of materials are used, is employed

for the solid layer.

First, the solid layer formation processing that can be employed for this invention will be described while referring to FIGS. 4A to 4F.

5 As shown in FIG. 4A, a positive type resist layer 12 that contains polymethylisopropenylketone (PMIPK) as a resin element is deposited on a substrate 11. Specifically, an ODUR positive type resist is applied by spin coating, and is prebaked at
10 120°C for three minutes. Then, the structure is baked at 150°C for 30 minutes. The film thickness at this time is 15 μm . Thereafter, in order to prevent the outer edge of a wafer from being raised, Deep UV light is projected through a wafer outer edge
15 exposure mask (not shown) onto only the outer edge of the wafer using UX-3000SC, by Ushio Inc., and the positive type resist raised at the outer edge of the wafer is developed and removed. Sequentially, as shown in FIG. 4B, a positive type resist layer 13
20 that contains a copolymer (P(MMA-MAN)) of methacrylic anhydride and methyl methacrylate as a resin element is formed on the ODUR positive type resist layer 12 using spin coating. During this process, the same positive type resist composite is employed as is used
25 for the first embodiment. The film thickness is 6 μm .

Following this, as shown in FIG. 4C, the positive type resist layer 13 is exposed, while a

photomask 16, with which exposed portions are to be removed, is employed for the positive type resist layer 13. At this time, when an area of 230 to 260 nm is designated as the exposure wavelength area, the lower positive type resist layer is nearly not exposed to light. This is because absorption of ketone is due to a carbonyl group, and almost all the light in the 230 to 260 nm area is transmitted through.

10 The exposed positive type resist layer 13 is developed using an alkaline liquid mixture of diethylene glycol, morpholine, monoethanolamine and pure water, and a predetermined pattern is obtained. With this alkaline development liquid, the speed of dissolution of the acrylic resist of the non-exposed portion can be greatly reduced, and the affect on the lower layer, during the development of the upper layer, less significant.

Next, as shown in FIG. 4D, post-baking is performed for the entire substrate at 130°C for three minutes, so that side walls, tilted at about 10°, can be formed on the upper positive type resist layer 13. Thereafter, as shown in FIG. 4E, the positive type resist layer 12 is exposed, while a photomask 17, with which exposed portions are to be removed, is employed for the positive type resist layer 12. At this time, when the wavelength of 270 to 330 nm has

been designated as the exposure wavelength, the lower positive type resist layer 12 can be exposed. Since the exposure wavelength of 270 to 330 nm is transmitted through the upper, positive type resist layer, almost no affect is produced by light entering through the mask or light reflected at the substrate.

Finally, as shown in FIG. 4F, the exposed, lower positive type resist layer 12 is developed, and a predetermined pattern wherein the lower layer and the upper layer are laminated like steps is obtained. In this lamination structure, the lower face of the upper layer is positioned within the upper face of the lower layer, and one part of the upper face of the lower layer is exposed. Methyl isobutyl ketone, which is an organic solvent, is appropriate for the development liquid. Since the non-exposed P(MMA-MAN) is nearly not dissolved by this liquid, the upper layer pattern is not changed during the development of the lower resist layer.

While referring to FIGS. 5A to 5H, an explanation will now be given for a liquid discharge head manufacturing method according to this embodiment that employs the solid layer shown in FIGS. 4A to 4F. FIGS. 5A to 5H are cross-sectional views of the ink flow path forming processing according to the second embodiment.

Since a driver and a logic circuit, for

controlling a discharge energy generation device 11a, are produced by a general semiconductor manufacturing method, it is appropriate that, as shown in FIG. 5A, silicon be used for a substrate 11. Further, a YAG
5 laser or a technique such as sand blasting may be employed to form ink supply through holes in a silicon substrate. However, it is preferable that the through holes not be present when the resist is coated, and as such a method, the silicon anisotropic
10 etching technique using an alkaline solution can be employed. In this case, a mask pattern 15 of, for example, alkali-resisting silicon nitride need only be formed on the reverse face of the substrate, and a membrane film (not shown) of the same material need
15 only be formed as an etching stopper on the obverse face of the substrate.

Sequentially, as shown in FIG. 5B, a positive type resist layer (ODUR layer) 12 containing PMIPK is deposited on the substrate 11. This deposition can
20 be performed using common spin coating. The film thickness is 14 μm .

Then, as shown in FIG. 5C, a positive type resist layer (P(MMA-MAN) layer) 13 of 6 μm thick is formed on the ODUR layer 12 using spin coating.
25 Following this, the P(MMA-MAN) layer 13 is exposed to obtain a structure shown in FIG. 5D. As previously described, a photomask with which the exposed

portions are to be removed is employed for the P(MMA-MAN) layer 13. At this time, when the wavelength area of 230 to 260 nm is designated as the exposure wavelength area, the lower positive type resist layer 5 12 is almost not exposed. This is because the absorption of ketone is due to a carbonyl group, and light of 230 to 260 nm is almost all transmitted through. The exposed P(MMA-MAN) layer 13 is developed by an alkaline liquid mixture of diethylene 10 glycol, morpholine, monoethanolamine and pure water, and a predetermined pattern is obtained. With this development liquid, the dissolving speed of the acrylic resist of the non-exposed portion can be lowered greatly, and the affect on the lower layer 15 during the development of the upper layer less significant.

Next, to obtain a structure shown in FIG. 5E, the ODUR layer 12 is exposed, while a photomask with which exposed portions are to be removed is employed 20 for the ODUR layer 12. At this time, when the wavelength of 270 to 330 nm is designated as the exposure wavelength, the lower positive type resist layer can be exposed. Further, since the exposure wavelength of 270 to 330 nm is transmitted through 25 the upper positive type resist layer 13, there is almost no affect incurred by light entering from the mask or light reflected from the substrate.

Thereafter, the lower positive resist layer 12 is developed, and a predetermined pattern is obtained. Methyl isobutyl ketone, which is an organic solvent, is appropriate for the development liquid. Since the non-exposed P(MMA-MAN) is nearly not dissolved by this liquid, the pattern of the upper layer 13 is not changed during the development of the lower resist pattern 12.

Following this, as shown in FIG. 5F, a curable composite is coated as a nozzle formation material to cover the lower ODUR layer 12 and the upper P(MMA-MAN) layer 13, and is used as a coated resin layer 14. A common solvent coating method, such as spin coating, can be employed as a coating method.

Resin composite 1 used in the first embodiment of this invention is dissolved in a solvent mixture of methyl isobutyl ketone and xylene at a density of 60 mass%, and the resultant mixture is applied using spin coating. The thickness of the obtained film on the substrate 11 is 25 μm . Then, pattern exposure for formation of ink discharge ports is performed by MPA-600FA, by Canon Inc. It should be noted that exposure is performed using 2.5 J/cm² and PEB is performed at 90°C for four minutes. Sequentially, a development process is performed using methyl isobutyl ketone/xylene to form ink discharge ports. In this embodiment, a discharge port pattern of $\phi 8 \mu\text{m}$

is formed. When a repellent film is to be deposited on the discharge port formation material, as described in Japanese Patent Laid-Open Application No. 2000-326515, a photosensitive repellent layer 14a need only be deposited and be collectively exposed and developed. At this time, the photosensitive repellent layer 14a can be deposited by laminating, spin coating, slit coating or spraying. Thereafter, the nozzle formation material 14 and the photosensitive repellent layer 14a are exposed at the same time. Since generally nozzle formation material 14 having a negative type characteristic is used, a photomask 18 is employed that prevents a discharge port portion from being exposed to light. And the layer of the discharge port formation material 14 is developed and a discharge port 15 is formed. It is preferable that an aromatic solvent, such as xylene, be employed for development. Next, as shown in FIG. 5G, by using OBC, marketed by Tokyo Ohka Kogyo Co., Ltd., a cyclized isoprene 19 is coated on the discharge port formation material layer in order to protect this material layer from an alkaline solution. Thereafter, the silicon substrate 11 is immersed in a tetramethylammonium hydride solution (TMAH) having a 22 mass% at 83°C for 13 hours, and a through hole 20 for ink supply is formed in the silicon substrate 11. Further, silicon nitride 15, which is used as a mask

and as a membrane to form an ink supply hole, is patterned in advance in the silicon substrate 11. Sequentially, after the anisotropic etching has been performed, the silicon substrate is mounted on a dry etching apparatus with the reverse face on top, and the membrane film is removed by an etchant wherein oxygen at 5% is mixed with CF_4 . Then, the silicon substrate 11 is immersed in xylene to remove OBC.

Therefore, by exposing the overall structure, the positive type resist layer (ODUR layer and the P(MMA-MAN) layer), which is the mold for flow paths is decomposed. When light having a wavelength of 330 nm or lower is projected, the resist materials of the upper and lower layers are decomposed into low-molecular compounds, and easily removed by a solvent. Finally, the positive type resist layer, which is the mold for flow paths is removed by a solvent. Through this processing, a flow path 21 communicating with the discharge port 15 is formed, as shown in the cross section in FIG. 5H. The flow path 21 in this invention is one part of a flow path pattern, and is so shaped that the height of the flow path 21 is low near a discharge chamber, which is a bubble generation chamber that contacts a heater 11a (liquid discharge energy generation section) 11a. When ultrasonic or megasonic vibration is applied at the step of removing the mold using a solvent, the

dissolving and removal period can be reduced.

The thus obtained ink jet recording head was mounted to a recording apparatus, and recording was performed using ink consisting in the pure state of diethylene glycol/isopropyl alcohol/isopropyl alcohol/lithium acetate/black dye food black 2 = 79.4/15/3/0.1/2.5. Compared with the conventional structure (the lower layer: P(MMA-MAN), the upper layer: PMIPK, no reaction inhibition material), the amount of ink discharged in this embodiment was increased by about 20%, stable printing was performed, and high quality printed matter was obtained. When the ink jet recording head for this embodiment was disassembled, scum could not be found through observation by the SEM, while in the conventional example, scum of several μm was observed along the flow paths.

As is described above, according to this embodiment, the above described shortcomings can be solved by the ink jet recording head manufacturing method that, at the least, comprises the steps of: coating and patterning, on a substrate including ink discharge means, two removable resin layers used to form ink flow paths; coating and patterning a discharge port formation material used to form ink flow paths and ink discharge ports; removing the removable resin; and using an ink jet recording head

for which the nozzle formation material, at the least, contains a cationically polymerizable chemical compound, a cationic photopolymerization initiator and an inhibitor of cationic photopolymerization.

5 Specifically, the cationic photopolymerization initiator generates cations upon irradiation with light, and the cations produce ring-opening polymerization of the epoxy ring of the epoxy resin, so that curing occurs based on the cationic addition
10 polymerization reaction. However, when an inhibitor of cationic photopolymerization, such as a nitrogen-containing compound, is present, this inhibitor forms a strong ion pair with generated cations, and in this case, the ring-opening polymerization of the epoxy
15 ring is halted. Thus, when the inhibitor of cationic photopolymerization is appropriately mixed, a curing speed for the exposed portion can be arbitrarily controlled, and a desired cured state can be precisely obtained. Furthermore, at the interface
20 between the exposed portion and the non-exposed portion, the curing condition is suppressed or is insufficient, depending on the amount of light that has reached the interface, or the amount of cations that are generated at the interface, or are dispersed
25 from the exposed portion, and the occurrence of a compatible layer is also suppressed. Therefore, the occurrence of the scum described above can be

prevented.

(Third Embodiment)

FIGS. 6A to 6G are diagrams showing the structure of a liquid ejection recording head and the manufacturing processing according to a third embodiment of the invention. In this embodiment, a liquid ejection recording head having two orifices (discharge ports) is shown. However, the same processing is performed for a high-density multi-array liquid ejection recording head having more orifices. In the third embodiment, a substrate 202 is employed that is made, for example, of glass, ceramics, plastic or metal, as shown in FIG. 6A. FIG. 6A is a schematic perspective view of a substrate before a photosensitive material layer is formed.

So long as the substrate 202 functions as a part of a wall member for a flow path, and as a support member for a flow path structure made of a photosensitive material layer that will be described later, the shape and the material of the substrate 202 are not especially limited. A desired number of liquid discharge energy generation devices (liquid discharge energy generating elements) 201, such as electro-thermal conversion devices or piezoelectric devices, are arranged on the substrate 202 (two in FIG. 6A). The array density is a pitch of 600 dpi or 1200 dpi. Discharge energy for discharging small

liquid droplets is applied to ink by the liquid discharge energy generation devices 201, and recording is performed. When electro-thermal conversion devices are employed as the liquid discharge energy generation devices 201, these devices heat the nearby recording liquid and generate and discharge energy. Or, when piezoelectric devices are employed, discharge energy is generated by the mechanical vibration of these devices. It should be noted that control signal input electrodes (not shown) for driving these devices are connected to the devices 201. Further, generally, various function layers, such as a protective layer, are formed in order to extend the life expectancy of these discharge energy generation devices 201, and also in this invention, these function layers can be provided naturally.

Most commonly, silicon is employed for the substrate 202. That is, since a driver and a logic circuit that controls discharge energy generation devices are produced using a common semiconductor manufacturing method, it is appropriate for silicon to be employed for the substrate. Further, a YAG laser or a sandblasting technique can be employed for forming ink supply through holes in the silicon substrate. However, when a heat-bridge type resist is employed as a lower layer material, the pre-bake

temperature for the resist is extremely high, as described above, and greatly exceeds a glass transition temperature for a resin, and during prebaking, the resin coated film hangs down into the
5 through hole. Therefore, it is preferable that through holes not be formed during the resist coating process. For this method, the silicon anisotropic etching technique using an alkaline solution can be employed. In this case, a mask pattern made, for
10 example, of alkaline-resisting silicon nitride must only be formed on the reverse face of the substrate, and a membrane film of the same material must be formed on the obverse face as an etching stopper.

Following this, as shown in FIG. 6B, a positive
15 type resist layer 203 is formed on the substrate 202 including the liquid discharge energy generation devices 201. This material is a copolymer of methyl methacrylate (MMA) and methacrylic anhydride (MAN) at a ratio of 90:10, and the weight-average molecular
20 weight (Mw) is 30000, while the degree of dispersion (Mw/Mn) is 3.46. The absorption spectrum for P(MMA-MAN), which is a positive type resist material for forming a mold, is shown in FIG. 2. As is shown in
FIG. 2, since the absorption spectrum for the
25 positive type resist material is present in the area for 260 nm or lower, even when radiated by a wavelength of 260 nm or higher, the molecules of the

materials are not excited in the pertinent energy area, and accordingly, a decomposition reaction is not accelerated. That is, the decomposition reaction of the positive type resist material is accelerated only by an ionizing radiation of 260 nm or lower, and at the succeeding development step, pattern formation can be performed. The particles of this resin are dissolved in diglyme at a solid content density of about 30 WT%, and the resultant liquid is used as a resist liquid. The viscosity of the coating solution at this time is about 600 cps. The resist liquid is applied to the substrate using spin coating, and the whole substrate is prebaked at 120°C for three minutes and is then primarily cured in an oven at 150°C for six minutes. The thickness of the thus obtained film is 15 μm .

Following this, as shown in FIG. 6C, patterning (exposure and development) of the positive type resist layer is performed. The exposure process is performed with a first wavelength of 210 to 330 nm, shown in FIG. 7. Although light of 260 nm or higher is irradiated, this light does not contribute to the decomposition reaction of the positive type resist layer. It is most appropriate to use a cut filter that blocks light of 260 nm or higher. During the exposure process, the positive resist layer is exposed to ionizing radiation through a photomask on

which a desired pattern is drawn. When an exposure apparatus including a projective optical system that has no affect on diffracted light is employed, mask design while taking convergence into account is not
5 required.

Sequentially, as shown in FIG. 6D, a resin composite used in the first embodiment is employed to deposit a discharge port formation layer 204 used to form nozzles, so that the patterned positive type
10 resist layer is covered.

The coating process is performed using spin coating, and the prebaking process is performed using a hot plate at 90°C for three minutes.

Following this, as shown in FIG. 6D, pattern
15 exposure and development of an ink discharge port are performed for the discharge port formation layer 204 using a mask 205. An arbitrary exposure apparatus can be employed so long as it can irradiate general UV light, and there is no restriction on the upper
20 limit of the wavelength area of irradiated light A so long as the wavelength area is 290 nm or higher and the negative type coated resin can react to the light. During the exposure process, a mask is employed that prevents radiation of light from a portion that is to
25 be an ink discharge port. The exposure is performed using Mask aligner MPA-600 Super, by Canon Inc., with 1000 mJ/cm². As shown in FIG. 3, the above described

exposure apparatus (E) radiates UV light of 290 to 400 nm, and within this area, the negative type coated resin has a photosensitive characteristic. When this exposure apparatus is employed, as shown in FIG. 6D, the pattern for the positive type resist layer formed in FIG. 6B is also exposed, through the negative type coated resin, to the UV light of 290 to 400 nm. Therefore, since the positive type resist material used in this invention reacts only to DeepUV light of 260 nm or lower, the decomposition reaction of the material is not accelerated at this step.

Thereafter, as shown in FIG. 6E, for development, the entire substrate is immersed in xylene for sixty seconds, and is then baked, at 100 °C, for one hour to increase the adhesion between the materials in the flow path structure. Sequentially, although not shown, a cyclized isoprene is coated on the flow path structure material layer to protect the material layer from an alkaline solution. For this material, OBC marketed by Tokyo Ohka Kogyo Co., Ltd. is employed. Then, the silicon substrate is immersed in a tetramethylammonium hydride (TMAH) solution of 22 mass% at 83°C for 14.5 hours, and through holes (not shown) for ink supply are formed. Further, silicon nitride, used as a mask and a membrane for forming ink supply holes, is patterned in advance in the silicon substrate. After this anisotropic

etching has been completed, the silicon substrate is mounted on a dry etching apparatus with the reverse face on top, and the membrane film is removed by an etchant wherein oxygen, 5%, is mixed with CF_4 . Then, 5 the silicon substrate is immersed in xylene to remove the OBC.

Next, as shown in FIG. 6F, by using a low pressure mercury lamp, ionizing radiation B within the wavelength area 210 to 330 nm is projected onto 10 the entire flow path structure material 207, and the positive type resist is decomposed. Thereafter, the silicon substrate is immersed in methyl lactate to collectively remove the mold pattern made of the positive type resist, as shown in the vertical cross- 15 sectional view in FIG. 6G. At this time, the silicon substrate is placed in a megasonic tub of 200 MHz in order to reduce the elution time. Through this process, an ink flow path 211 including a discharge port is formed, and thus, an ink discharge element is 20 obtained wherein ink from an ink supply hole 210 is introduced to the ink flow path 211 and is discharged from a discharge port 209 by a heat generation device 202. The size of the obtained discharge port 209 is $\phi 8 \mu\text{m}$, the OH height is $20 \mu\text{m}$, and the OP thickness 25 is $5 \mu\text{m}$. Further, there is no occurrence of the above-described scum.

When the thus obtained discharge element was

mounted on an ink jet head unit shown in FIG. 8, and a recording evaluation was performed, satisfactory image recording was enabled. As one mode for this ink jet head unit, as shown in FIG. 8, for example, a
5 TAB film 214 that exchanges record signals with the main body of a recording apparatus is provided on the outer face of a holding member that supports a detachable ink tank 213, and an ink discharge element 212 is mounted on the TAB film 214 and is connected
10 to electrical wiring by electrical connection leads 215.

(Fourth Embodiment)

FIGS. 9A to 9I are diagrams showing the structure of a liquid ejection recording head
15 according to a fourth embodiment of the present invention, and a manufacturing method therefor. In this embodiment, a liquid ejection recording head having two orifices (discharge ports) is shown; however, the same processing is applied for a high-
20 density multi-array liquid ejection recording head having more than two orifices.

In the fourth embodiment, a substrate 201 is employed that is made, for example, of glass, ceramics, plastic or metal, as shown in FIG. 9A. FIG.
25 9A is a schematic perspective view of a substrate before a photosensitive material layer is formed. So long as the substrate 201 functions as a part of a

wall member for a flow path, and as a support member for a flow path structure made of a photosensitive material layer that will be described later, the shape and the material of the substrate 201 are not especially limited. A desired number of liquid discharge energy generation devices (liquid discharge energy generating elements) 202, such as electro-thermal conversion devices or piezoelectric devices, are arranged on the substrate 201 (two in FIG. 9A).

Discharge energy for discharging small liquid droplets is applied to ink by the liquid discharge energy generation devices 202, and recording is performed. When electro-thermal conversion devices are employed as the liquid discharge energy generation devices 202, these devices heat the recording liquid nearby and generate discharge energy. Or, when piezoelectric devices are employed, discharge energy is generated by mechanical vibration of these devices.

It should be noted that control signal input electrodes (not shown) for driving these devices are connected to the discharge energy generation devices 202. Further, generally, various function layers, such as a protective layer, are formed in order to extend the life expectancy of these discharge energy generation devices 202, and also, naturally, in this invention, these function layers can be provided.

Most commonly, silicon is employed for the substrate 201. That is, since a driver and a logic circuit that controls discharge energy generation devices are produced by a common semiconductor manufacturing method, it is appropriate for silicon to be employed for the substrate. Further, a YAG laser or a sandblasting technique can be employed for forming ink supply through holes in the silicon substrate. However, it is preferable that through holes not be formed during the resist coating process. For this method, the silicon anisotropic etching technique that uses an alkaline solution can be employed. In this case, a mask pattern made, for example, of alkaline-resisting silicon nitride must only be formed on the reverse face of the substrate, and a membrane film of the same material must be formed on the obverse face as an etching stopper.

Sequentially, as shown in FIG. 9B, a PMIPK positive type resist layer 203 is coated on the substrate 201 on which the liquid discharge energy generation devices 202 are mounted. As PMIPK, the resin density of ODUR-1010 marketed by Tokyo Ohka Kogyo Co., Ltd., is adjusted to 20 WT%. The prebaking process is performed using a hot plate at 120°C for three minutes, and thereafter, the thermal process is performed in an oven, under a nitrogen atmosphere, at 150°C for 30 minutes. The thickness of

the deposited film is 15 μm .

Following this, as shown in FIG. 9C, a photodegradable positive type resist layer 204 of P(MMA-MAN) is applied to the positive type resist layer 203. The following positive resist is employed for the photodegradable positive type resist of P(MMA-MAN):

radical polymer (P(MMA-MAN) of methyl methacrylate and methacrylic acid, weight-average molecular weight (M_w : polystyrene conversion) = 30000, degree of dispersion (M_w/M_n) = 3.5

The particles of this resin are dissolved in a diglyme solvent having a solid content density of about 25 mass%, and the resultant liquid is used as a resist liquid. The viscosity of the resist solution at this time is 600 cps. The resist liquid is applied to the substrate using spin coating, and the entire substrate is prebaked at 100°C for three minutes, and is heated in an oven, under a nitrogen atmosphere, at 150°C for 30 minutes. The thickness of the thus formed resist layer, after the heat processing, is 5 μm .

Next, as shown in FIG. 9D, exposure is performed for the photodegradable positive resist layer 204 of P(MMA-MAN). Mask aligner UX-3000 SC, by Ushio Inc., is employed as an exposure apparatus, and light having an exposure wavelength of 230 to 260 nm

is selectively employed for irradiation by using a cut filter. Then, as shown in FIG. 9E, the photodegradable positive type resist layer 204 composed of P(MMA-MAN) is developed by using a development liquid having the following composition, and a desired pattern is formed.

Development liquid:

diethylene glycol monobutyl ether: 60 vol%

ethanol amine: 5 vol%

10 morpholine: 20 vol%

ion exchange water: 15 vol%

Next, as shown in FIG. 9F, patterning (the exposing and developing) of the lower positive resist layer 203 of PMIPK is performed. The same exposure apparatus is employed, and light having an exposure wavelength of 270 to 330 nm is employed to selectively perform irradiation using a cut filter. The development is made by methyl isobutyl ketone. Then, as shown in FIG. 9G, resin composite 1 used in the first embodiment is employed to form a discharge port formation layer 207, so that the lower positive type resist layer 203 and the upper positive type resist layer 204 that have been patterned are covered.

For forming this layer 207, resin composite 1 is dissolved in a solvent mixture of methyl isobutyl ketone and xylene at a density of 60 mass%, and the resultant liquid is applied to the substrate using

spin coating. The entire substrate is prebaked, using a hot plate at 90°C for three minutes. Mask aligner MPA-600 FA, by Canon Inc., is employed as an exposure apparatus, and an exposure of 3J/cm² is performed. The structure is thereafter immersed in xylene for sixty seconds for developing, and is then baked at 100°C for one hour in order to increase the adhesion of the discharge port formation material. Thereafter, the pattern exposure and development of an ink discharge port 209 is performed for the discharge port formation material 207. An arbitrary exposure apparatus can be employed for the pattern exposure, and although not shown, a mask that prevents light from being projected onto a portion that is to be an ink discharge port is employed during the exposure process.

Sequentially, although not shown, a cyclized isoprene is coated on the flow path structure material layer to protect the material layer from an alkaline solution. For this material, OBC, marketed by Tokyo Ohka Kogyo Co., Ltd., is employed. Then, the silicon substrate is immersed in a tetramethylammonium hydride (TMAH) solution having a 22 mass% at 83°C for 13 hours, and through holes (not shown) for ink supply are formed. Furthermore, silicon nitride, used as a mask and membrane for forming ink supply holes, is patterned in advance in

the silicon substrate. After this anisotropic etching has been completed, the silicon substrate is mounted on a dry etching apparatus with the reverse face on top, and the membrane film is removed using an etchant wherein oxygen, 5%, is mixed with CF_4 . Then, the silicon substrate is immersed in xylene to remove the OBC.

Next, as shown in FIG. 9H, by using a low pressure mercury lamp, ionizing radiation 208 in the wavelength area 300 nm or lower is projected onto the entire substrate through the discharge port formation material 207, and the upper positive type resist of PMIPK and the lower positive type resist of P(MMA-MAN) are decomposed. The amount of ionizing radiation is $50\text{J}/\text{cm}^2$.

Thereafter, the silicon substrate 201 is immersed in methyl lactate to collectively remove the mold resist, as shown in the vertical cross-sectional view in FIG. 9I. At this time, the silicon substrate 201 is placed in a megasonic tub of 200 MHz in order to reduce the elution time. Through this process, an ink flow path 211 including a discharge port is formed, and thus, an ink discharge element is obtained whereby ink from each ink flow path 211 is introduced to each discharge chamber through an ink supply hole 210, and is discharged from a discharge port 209 by a heater. The size of the obtained

discharge port 209 is $\phi 6 \mu\text{m}$, and the OH height is $25 \mu\text{m}$. Since the flow path height is $15 \mu\text{m}$, and the thickness of the P(MMA-MAN) film formed on the heater is $5 \mu\text{m}$, the OP thickness is $5 \mu\text{m}$. Further, no scum
5, described before is generated.

(Fifth Embodiment)

An ink jet head having the structure shown in FIG. 10 is manufactured using the method of the fourth embodiment of the present invention.

10 According to a fifth embodiment of this invention, as shown in FIG. 10, the horizontal distance (L) from an opening edge 310a of an ink supply port 310 to an end 311a of a discharge chamber 311 at an ink supply port side, is $80 \mu\text{m}$. An ink flow path wall 312 is formed
15 at a distance (312a) of $50 \mu\text{m}$ (I) toward the ink supply port 310 side from the end 311a of the discharge chamber 311 at the ink supply port side, and divides individual discharge elements. Further, the ink flow path height (H) is $15 \mu\text{m}$, and the
20 distance (OH) from the surface of a substrate 301 to the surface of a discharge port formation material 307 is $26 \mu\text{m}$. As shown in FIG. 10, the sizes of ink discharge ports 309a and 309b, arranged with the ink supply port located between them, are respectively $\phi 6 \mu\text{m}$ and $\phi 12 \mu\text{m}$, and heaters are arranged in consonance
25 with the amount of ink discharged. The amount of ink discharged by the individual discharge ports are 0.5

pl and 2.0 pl. 256 nozzles are arranged in a zigzag manner (not shown) at a pitch of 42.3 μm in the perpendicular direction relative to the plane of the paper in FIG. 10. It should be noted that in FIG. 10 reference numeral 302 denotes a heater and 307a denotes a beam provided for the discharge port formation material 307. The OP thickness (OP) is 5 μm .

(Sixth Embodiment)

10 An ink jet head having a structure shown in FIG. 11 is manufactured using the method according to the fourth embodiment. According to a sixth embodiment of the present invention, as shown in FIG. 11, the horizontal distance (L) from an opening edge 310a of an ink supply port 310 to an end 311a of a discharge chamber 311 at an ink supply port side, is 80 μm . An ink flow path wall 312 is formed at a distance (312a) of 50 μm (I) toward the ink supply port 310 side from the end 311a of the discharge chamber 311 at the ink supply port side, and separates individual discharge elements. Further, the ink flow path height (H) is 15 μm , and the distance (OH) from the surface of a substrate 301 to the surface of a discharge port formation material 307 is 25 μm . As shown in FIG. 11, the sizes of ink discharge ports 309a and 309b, arranged with the ink supply port located between them, are respectively $\phi 3 \mu\text{m}$ and $\phi 16 \mu\text{m}$, and heaters

are arranged in consonance with the amount of ink discharged. The amounts of ink discharged by the individual discharge ports are 0.2 pl and 5.0 pl. 256 nozzles are arranged in a zigzag manner (not shown) at a pitch of 42.3 μm , in the perpendicular direction relative to the plane of the paper in FIG. 11. It should be noted that in FIG. 11, reference numeral 302 denotes a heater, and 307a denotes a beam provided for the discharge port formation material 307. The OP thickness (OP) is 5 μm . (Seventh Embodiment)

An ink jet head having a structure shown in FIG. 12 is manufactured by the method according to the fourth embodiment. According to a seventh embodiment of the present invention, as shown in FIG. 12, the horizontal distance (L) from an opening edge 310a of an ink supply port 310 to an end 311a of a discharge chamber 311 at an ink supply port side is 80 μm . An ink flow path wall 312 is formed at a distance (312a) of 50 μm (I) toward the ink supply port 310 side from the end 311a of the discharge chamber 311 at the ink supply port side, and divides individual discharge elements. Further, the ink flow path height (H) is 15 μm , and the distance (OH) from the surface of a substrate 301 to the surface of a discharge port formation material 307 is 26 μm . As shown in FIG. 12, the sizes of ink discharge ports 309a and 309b

arranged with the ink supply port arranged between them are respectively $\phi 7 \mu\text{m}$ and $\phi 11 \mu\text{m}$, and heaters are arranged in consonance with the amount of discharged ink. The amounts of ink discharged by the individual discharge ports are 0.6 pl and 2.0 pl. 256 nozzles are arranged in a zigzag manner (not shown) at the pitch of $42.3 \mu\text{m}$ in the perpendicular direction relative to the plane of paper in FIG. 12. The OP thickness (OP) is $5 \mu\text{m}$.

As is described above, according to the present invention, since the inhibitor of cationic photopolymerization is mixed with a photocurable composite that is a discharge port formation material to be used through cationic polymerization, and a portion that is to be a discharge port and a solid layer that serves an interface are deposited using a copolymer of methacrylic anhydride and methyl methacrylate. Therefore, the manufacturing steps are substantially unchanged compared with the conventional steps, and an inexpensive ink jet head with no scum can be provided. Furthermore, two solid layers are provided, and a vinylketone photodegradable macromolecule compound or polymethylisopropenylketone is employed for the lower layer, while a copolymer of methacrylic anhydride and methacrylate ester is employed for the upper layer, and the discharge port formation material contains at

least a cationically polymerizable chemical compound,
cationic photopolymerization initiator and a
inhibitor of cationic photopolymerization. As a
result, an inexpensive liquid ejection head can be
5 provided for which the manufacturing steps are
substantially unchanged compared with the
conventional steps and no scum occurs, and wherein an
intermediate chamber that is smaller than the flow
path portion on the substrate side that reduces the
10 liquid flow resistance is accurately formed along the
flow path under the discharge port.

This application claims priority from Japanese
15 Patent Application No. 2004-190482 filed on June 28,
2004, which is hereby incorporated by reference
herein.

CLAIMS

1. A method for manufacturing a liquid discharge head comprising the steps of:

5 forming a solid layer for forming a flow path on a substrate on which an energy generating element is arranged to generate energy that is used to discharge liquid; forming, on the substrate where the solid layer is mounted, a coating layer for coating
10 the solid layer;

forming a discharge port used to discharge a liquid, through a photolithographic process, in the coating layer formed on the solid layer; and

removing the solid layer to form a flow path
15 that communicates with the energy element and the discharge port,

whereby a material used for the coating layer contains a cationically polymerizable chemical compound, cationic photopolymerization initiator and
20 a inhibitor of cationic photopolymerization, and

whereby a material of the solid layer that forms a boundary with a portion where the discharge port of the coating layer is formed contains a copolymer of methacrylic anhydride and methacrylate
25 ester.

2. A method according to claim 1, whereby the copolymer of methacrylic anhydride and methacrylate

ester has a weight-average molecular weight of 20000 to 100000 and a ratio of a content of methacrylic anhydride of 5 to 30 weight% relative to the copolymer.

5 3. A method according to claim 2, whereby the copolymer is a copolymer of methacrylic anhydride and methyl methacrylate.

 4. A method according to claim 1, whereby the inhibitor of cationic photopolymerization is a basic
10 material having a pair of nonshared electrons.

 5. A method according to claim 4, whereby the inhibitor of cationic photopolymerization is a nitrogen-containing compound having a pair of nonshared electrons.

15 6. A method according to claim 5, whereby the inhibitor of cationic photopolymerization is an amine compound.

 7. A method according to claim 1, whereby the step of forming the solid layer includes the steps
20 of:

 forming, on the substrate, a first positive type photosensitive material layer that is exposed to ionizing radiation of a first wavelength,

 forming, on the first positive type
25 photosensitive material layer, a second positive type photosensitive material layer that is exposed to ionizing radiation of a second wavelength that is

different from the first wavelength,

irradiating the ionizing radiation of the second wavelength to the substrate where the first and the second positive type photosensitive material layers are formed, and forming a desired pattern on the second positive type photosensitive material layer, and

irradiating the ionizing radiation of the first wavelength to the substrate where the first and the second positive type photosensitive material layers are formed, and forming a desired pattern on the first positive type photosensitive material layer; and whereby the second positive type photosensitive material layer forms the boundary with the coated layer.

8. A method according to claim 7, whereby a material for forming the first positive type photosensitive material layer contains polymethylisopropenylketone.

9. A liquid discharge head manufactured by a method according to one of claims 1 to 8, wherein a discharge port formation material used for forming a discharge port for the liquid discharge head contains a cationically polymerizable chemical compound, a cationic photopolymerization initiator and a inhibitor of cationic photopolymerization.

1 / 14

FIG. 1A

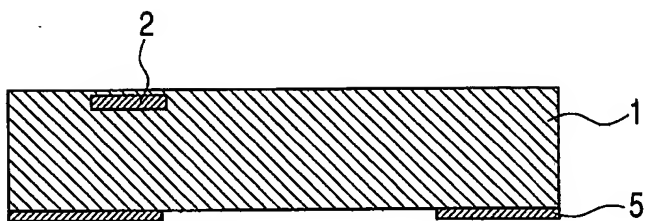


FIG. 1B

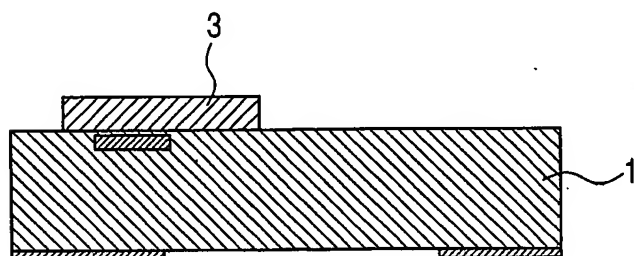


FIG. 1C

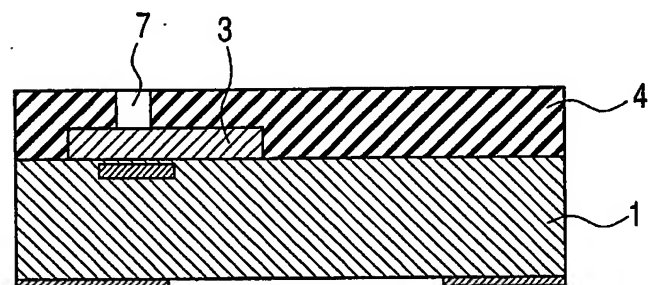


FIG. 1D

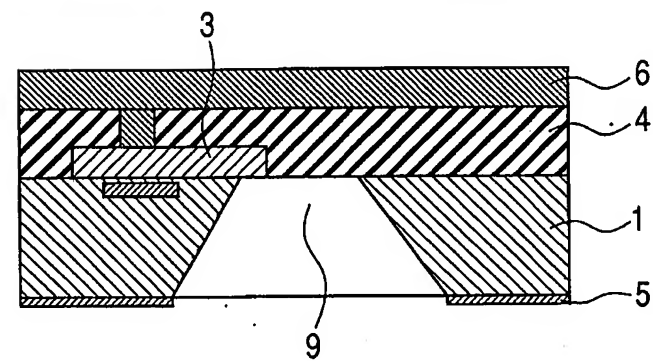
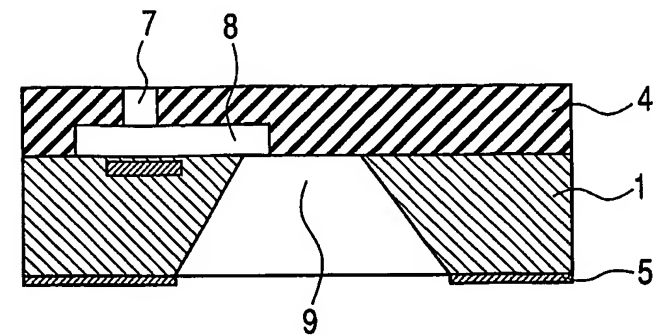
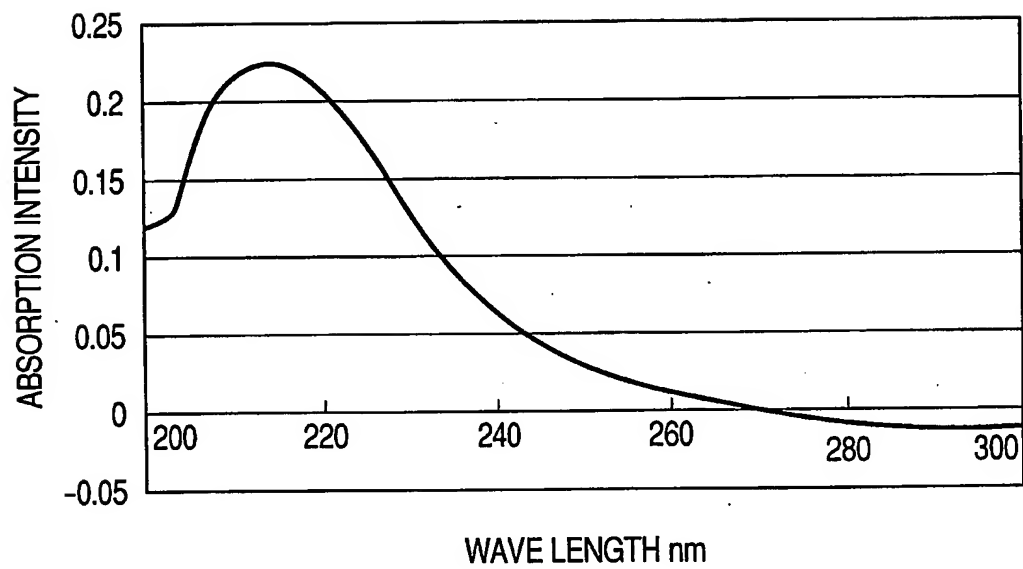


FIG. 1E

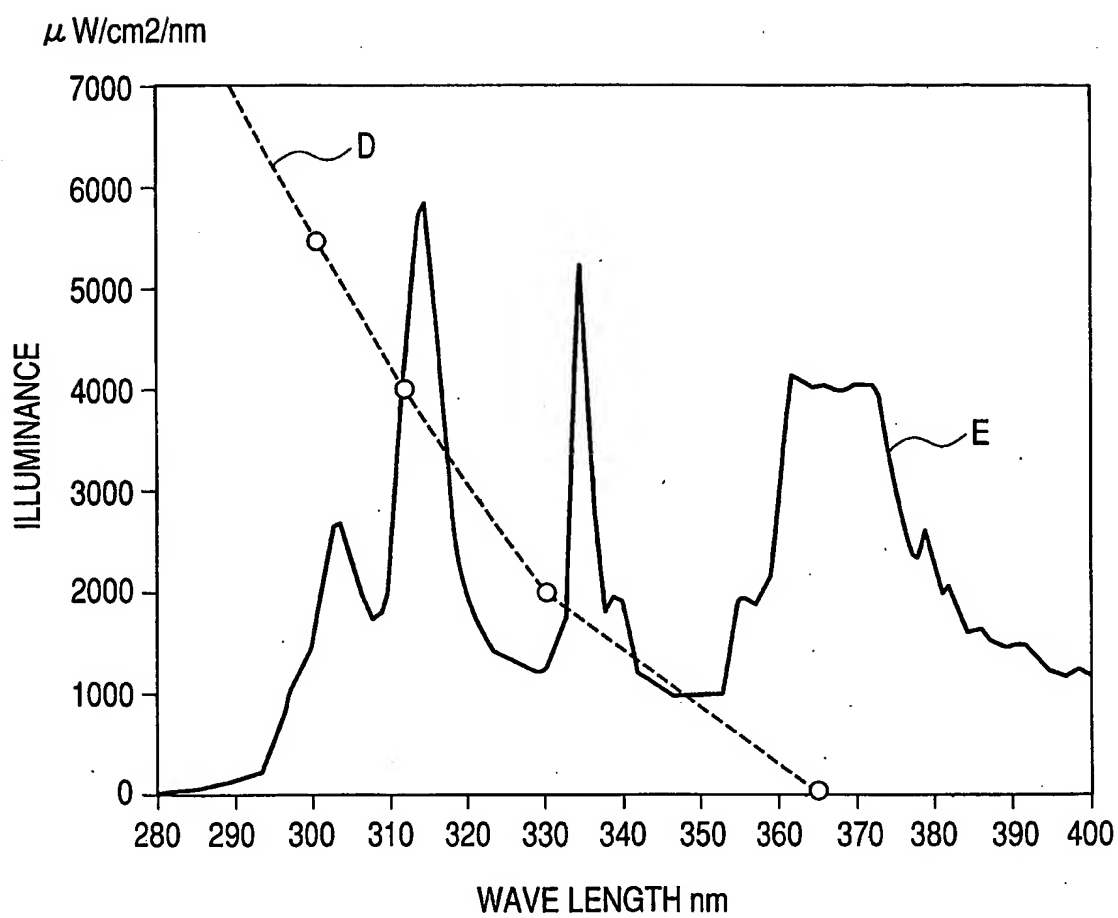


2 / 14

FIG. 2

3 / 14

FIG. 3



4 / 14

FIG. 4A



FIG. 4B



FIG. 4C

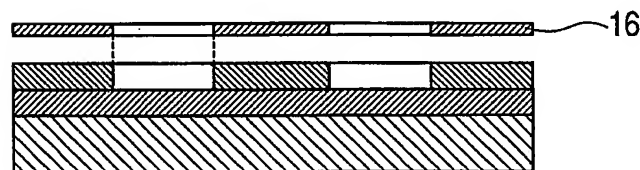


FIG. 4D



FIG. 4E

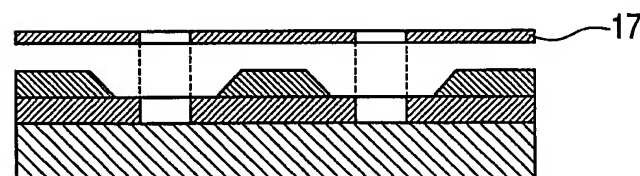


FIG. 4F

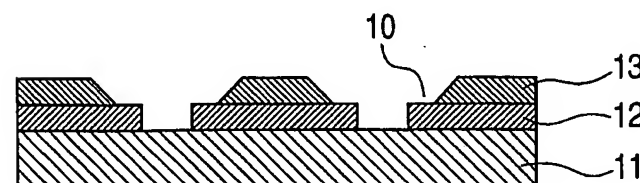


FIG. 5A

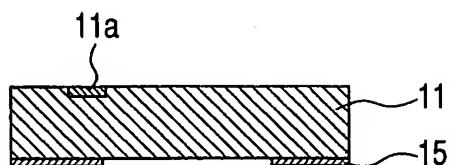


FIG. 5E

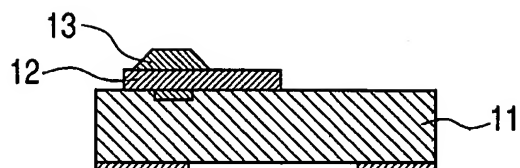


FIG. 5B

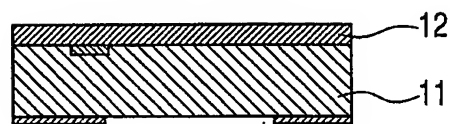


FIG. 5F

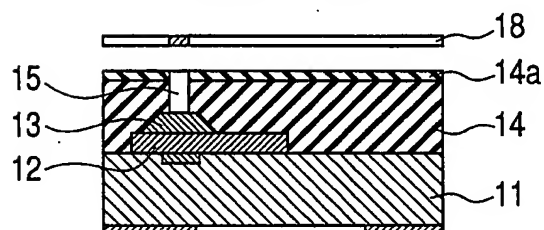


FIG. 5C

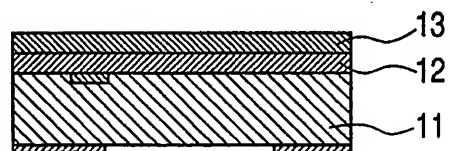


FIG. 5G

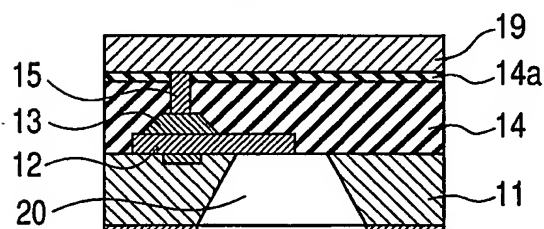


FIG. 5D

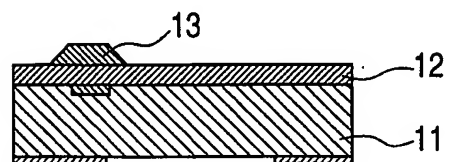
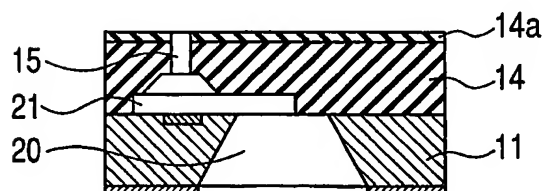


FIG. 5H



6 / 14

FIG. 6A

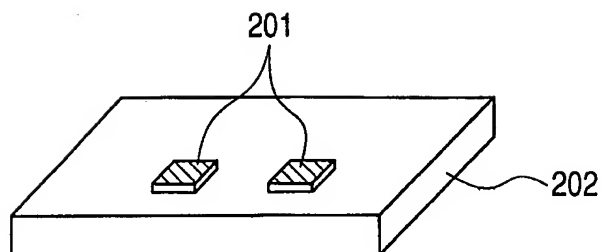


FIG. 6B

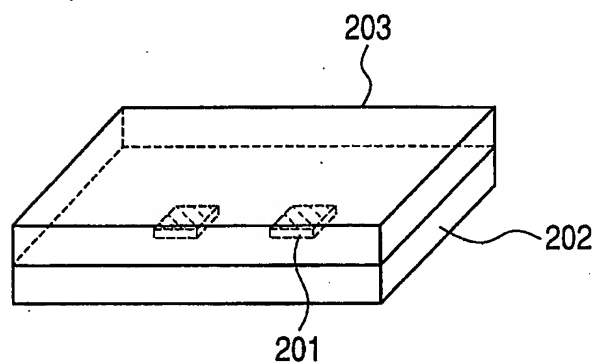


FIG. 6C

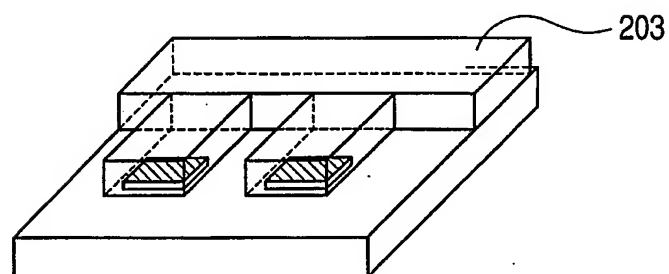
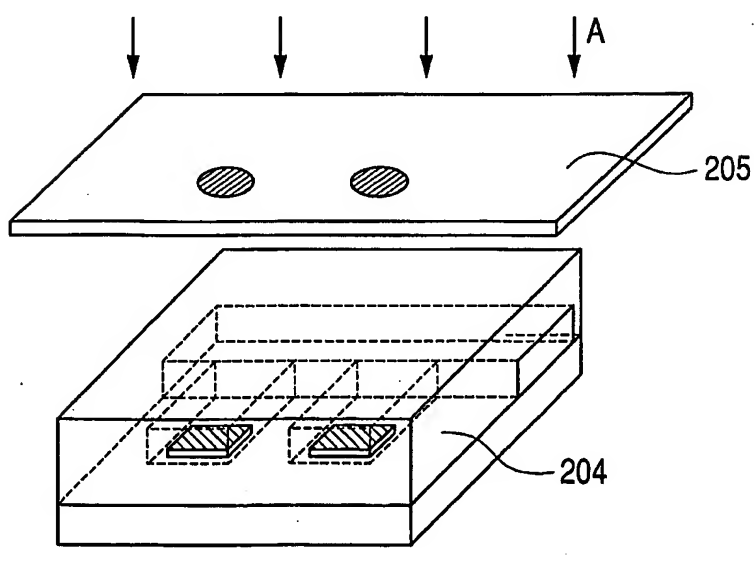


FIG. 6D



7/14

FIG. 6E

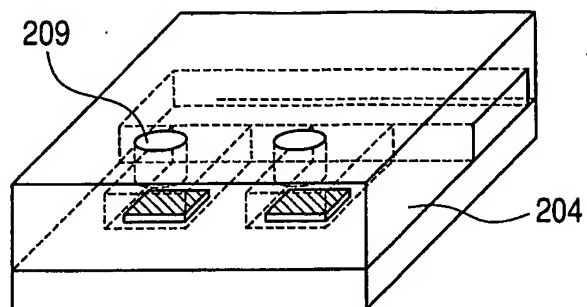


FIG. 6F

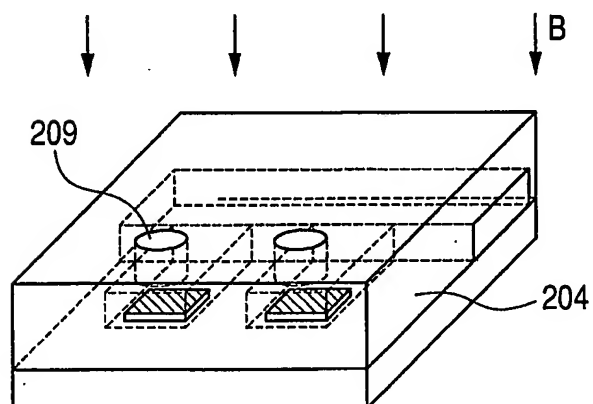
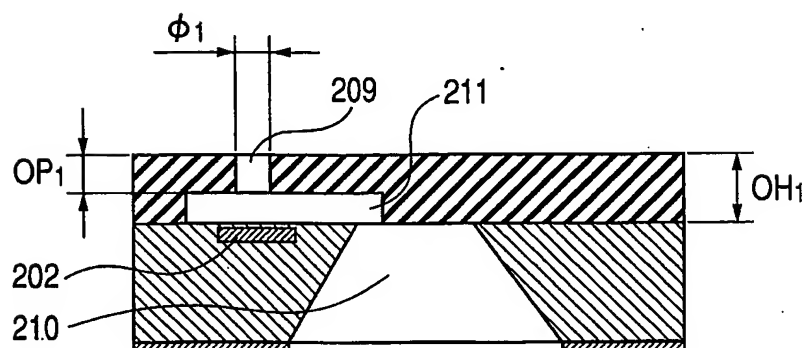


FIG. 6G



8/14

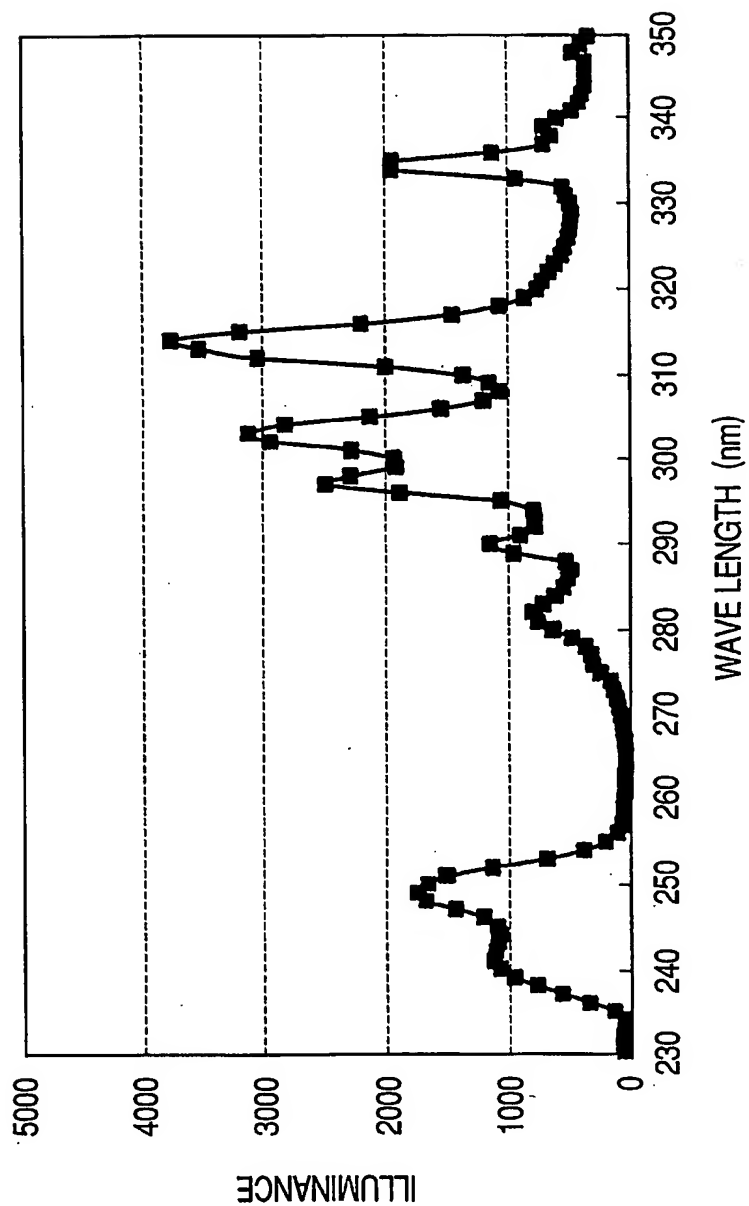
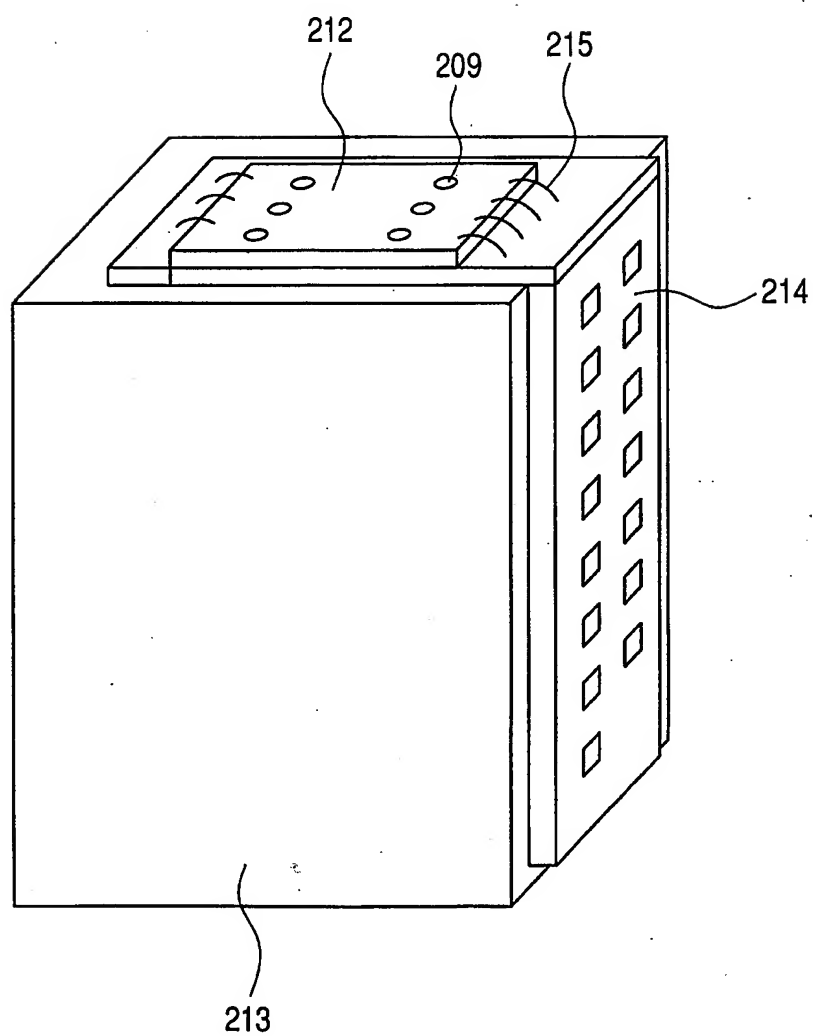
FIG. 7CORRELATION BETWEEN EXPOSURE
(DEEP UV EXPOSURE) & ILLUMINANCE

FIG. 8



10 / 14

FIG. 9A

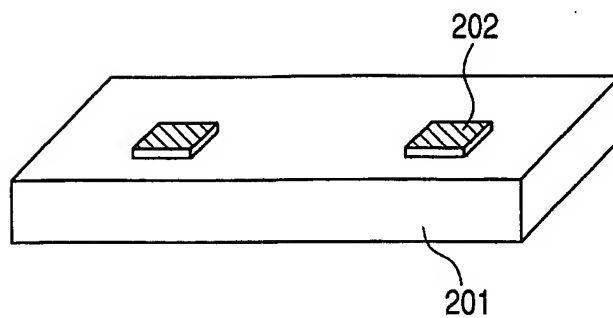


FIG. 9B

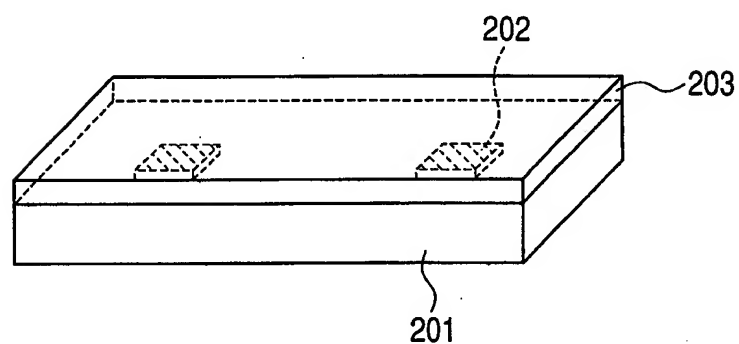


FIG. 9C

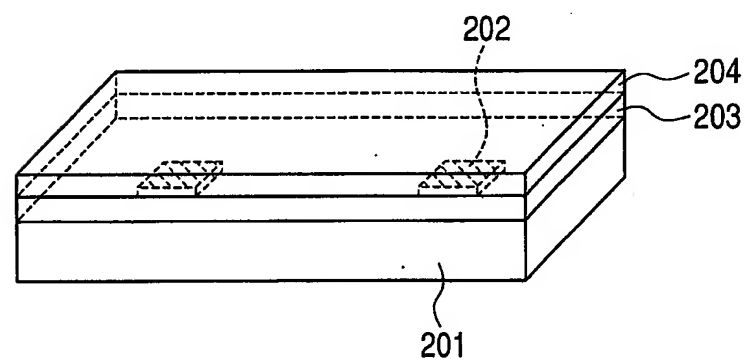


FIG. 9D

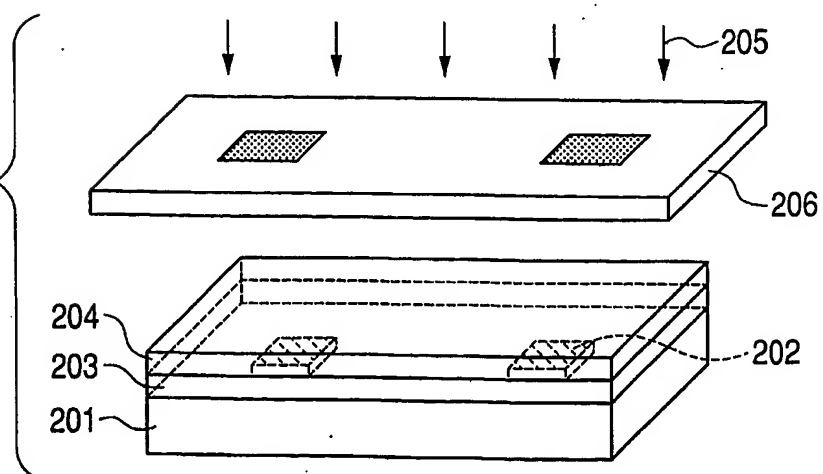


FIG. 9E

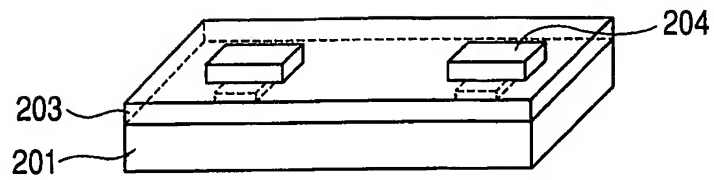


FIG. 9F

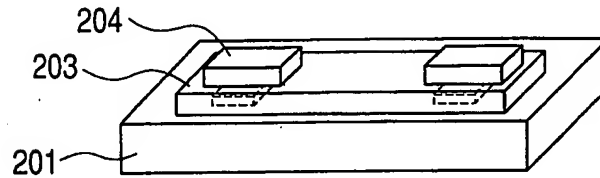


FIG. 9G

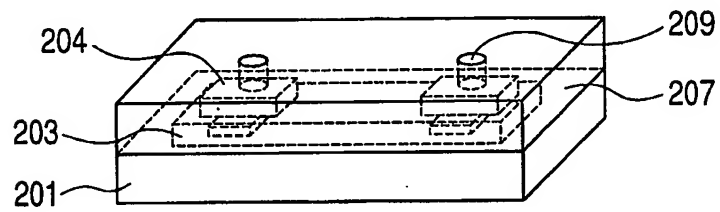


FIG. 9H

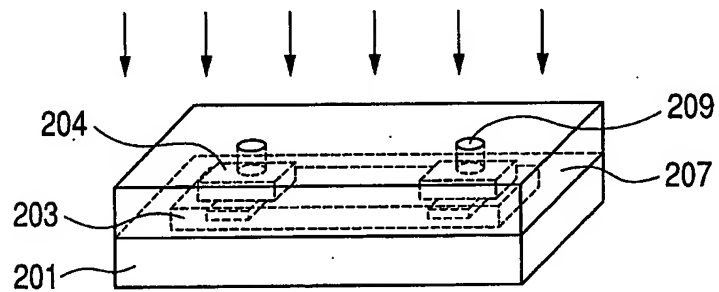


FIG. 9I

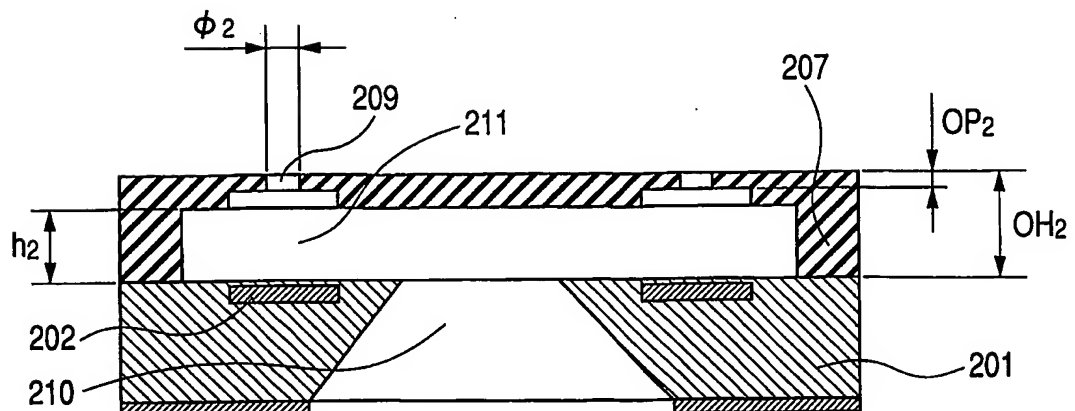


FIG. 10

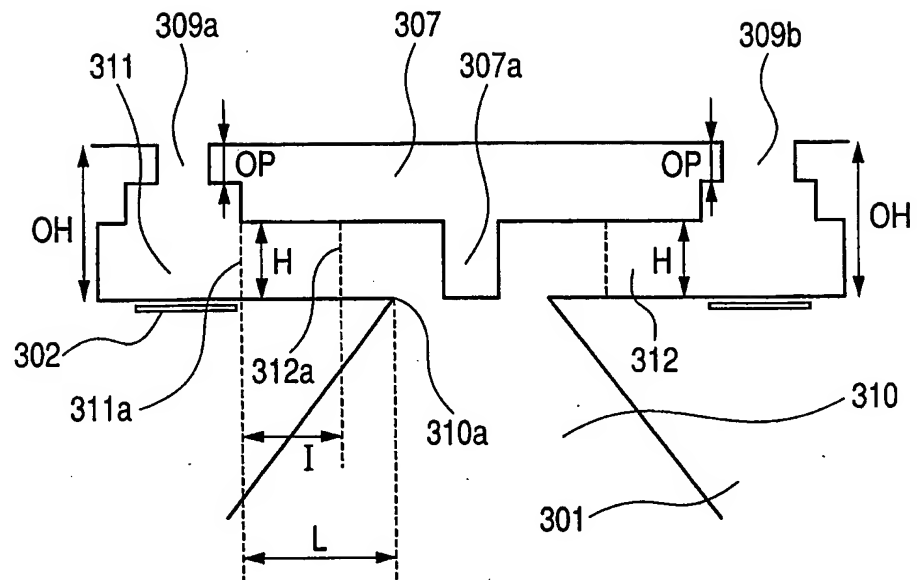


FIG. 11

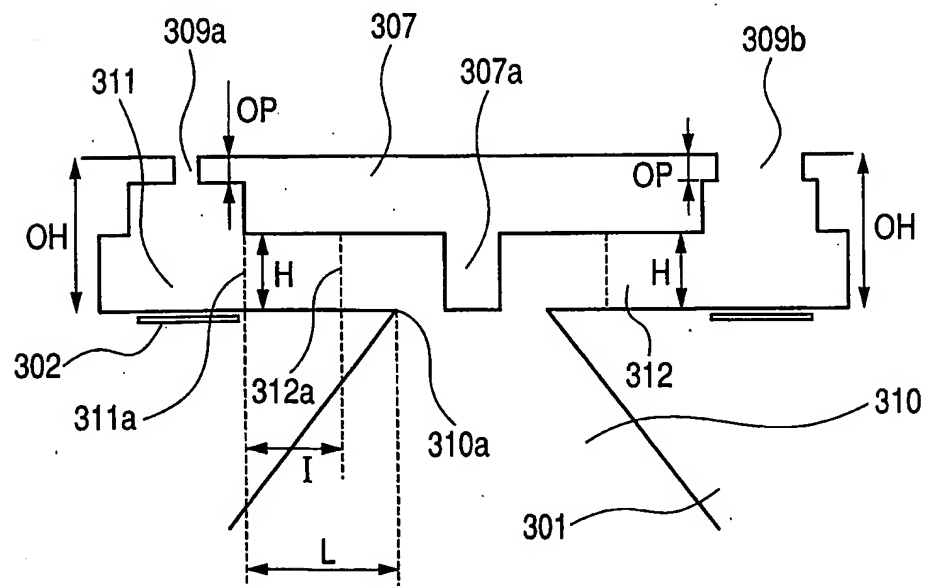


FIG. 12

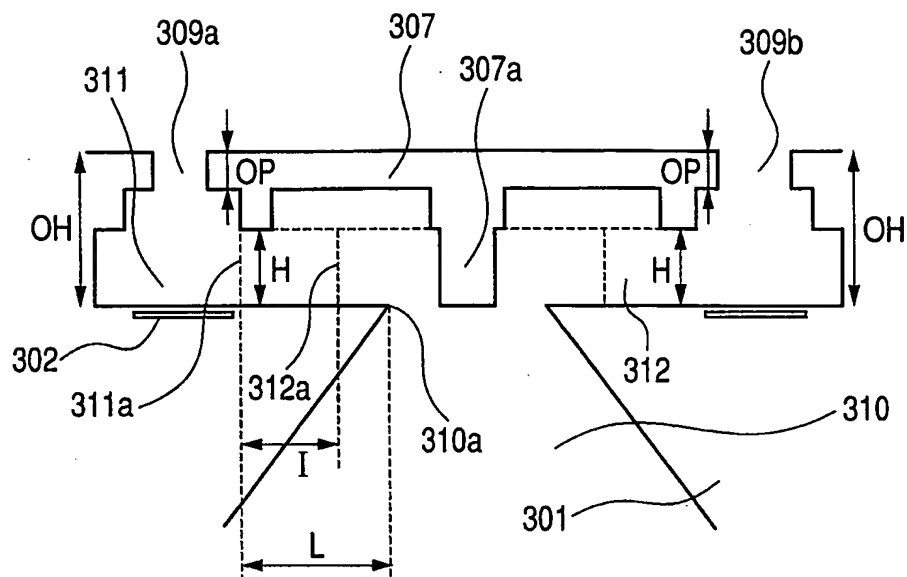


FIG. 13A

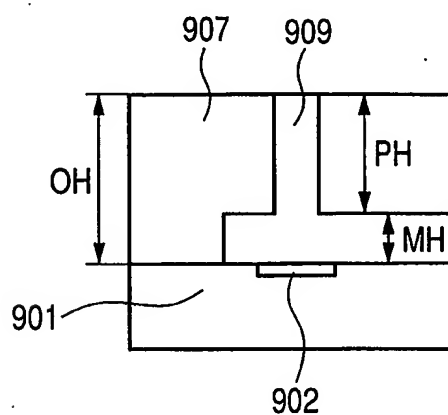


FIG. 13B

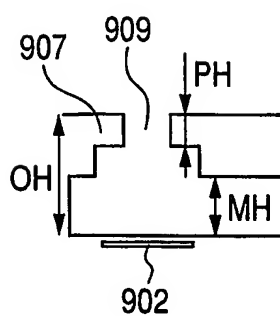
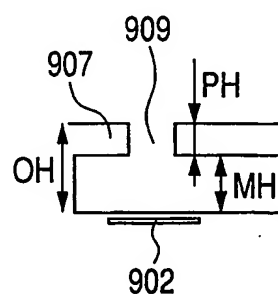


FIG. 13C



14 / 14

FIG. 14A

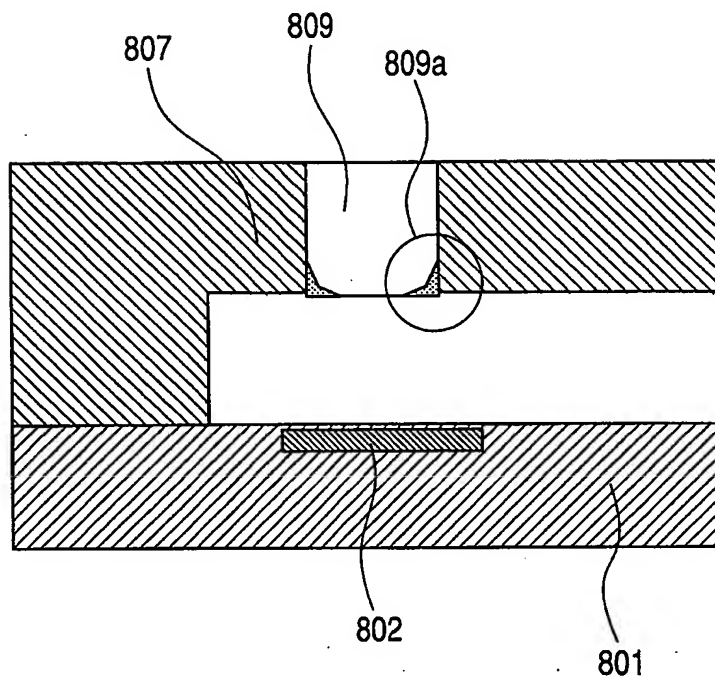
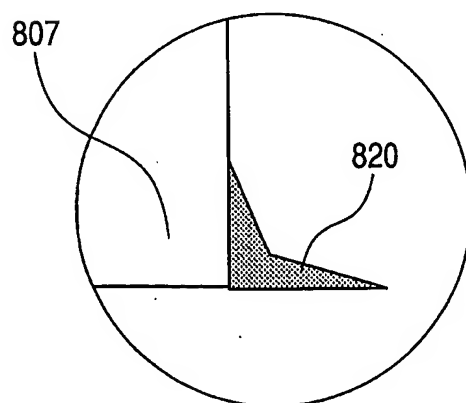


FIG. 14B



(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
5 January 2006 (05.01.2006)

PCT

(10) International Publication Number
WO 2006/001530 A3

- (51) International Patent Classification⁷: **B41J 2/16**,
G03F 7/00
- (21) International Application Number:
PCT/JP2005/012266
- (22) International Filing Date: 27 June 2005 (27.06.2005)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
2004-190482 28 June 2004 (28.06.2004) JP
- (71) Applicant (for all designated States except US): **CANON KABUSHIKI KAISHA** [JP/JP]; 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **KUBOTA, Masahiko** [JP/JP]; c/o CANON KABUSHIKI KAISHA, 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP). **SUZUKI, Takumi** [JP/JP]; c/o CANON KABUSHIKI KAISHA, 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP). **SATO, Tamaki** [JP/JP]; c/o CANON

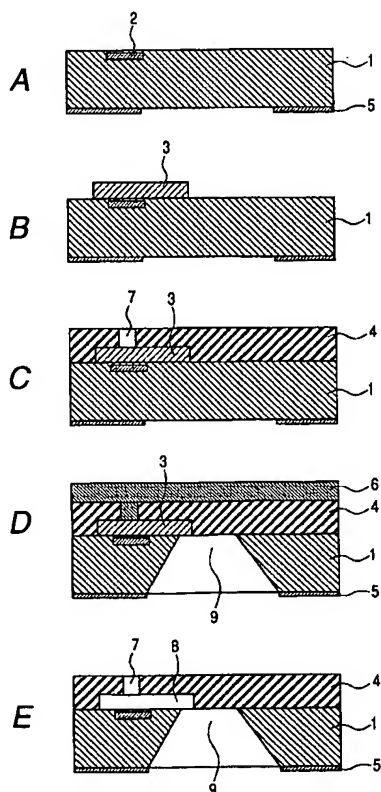
KABUSHIKI KAISHA, 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP). **KANRI, Ryoji** [JP/JP]; c/o CANON KABUSHIKI KAISHA, 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP). **HATTA, Maki** [JP/JP]; c/o CANON KABUSHIKI KAISHA, 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP). **ASAI, Kazuhiro** [JP/JP]; c/o CANON KABUSHIKI KAISHA, 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP). **SHIBA, Shoji** [JP/JP]; c/o CANON KABUSHIKI KAISHA, 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP). **HINO, Etsuko** [JP/JP]; c/o CANON KABUSHIKI KAISHA, 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP). **ISHIKURA, Hiroe** [JP/JP]; c/o CANON KABUSHIKI KAISHA, 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP). **OKANO, Akihiko** [JP/JP]; c/o CANON KABUSHIKI KAISHA, 3-30-2, Shimomaruko, Ohta-ku, Tokyo 1468501 (JP).

(74) Agents: **OKABE, Masao** et al.; No. 602, Fuji Bldg., 2-3, Marunouchi 3-chome, Chiyoda-ku, Tokyo 1000005 (JP).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

[Continued on next page]

(54) Title: **LIQUID DISCHARGE HEAD MANUFACTURING METHOD, AND LIQUID DISCHARGE HEAD OBTAINED USING THIS METHOD**



(57) Abstract: According to the present invention, a method for manufacturing a liquid discharge head includes the steps of depositing a solid layer (3) for forming a flow path on a substrate (1) on which an energy generating element (2) is arranged to generate energy that is used to discharge liquid, forming, on the substrate where the solid layer is mounted, a coating layer (4) for coating the solid layer, forming a discharge port (7) used to discharge a liquid, through a photolithographic process, in the coating layer formed on the solid layer, and removing the solid layer to form a flow path (8) that communicates with the energy element and the discharge port, whereby a material used for the coating layer contains a cationically polymerizable chemical compound, cationic photopolymerization initiator and an inhibitor of cationic photopolymerization, and whereby a material of the solid layer that forms a boundary with a portion where the discharge port of the coating layer is formed contains a copolymer of methacrylic anhydride and methacrylate ester.



AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

(88) Date of publication of the international search report:

23 February 2006

- (84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP2005/012266

A. CLASSIFICATION OF SUBJECT MATTER
B41J2/16 G03F7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B41J G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 1 380 425 A (CANON KABUSHIKI KAISHA) 14 January 2004 (2004-01-14) paragraphs '0036! - '0038!, '0041! paragraphs '0052! - '0064! paragraphs '0078! - '0094! figures 1A-2D, 10-18	1-9
Y	EP 1 380 423 A (CANON KABUSHIKI KAISHA) 14 January 2004 (2004-01-14) paragraphs '0020! - '0022! paragraphs '0026!, '0028!, '0033! - '0064! figures 1A-1E, 5-12 ----- -/-	1-6, 9

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

16 November 2005

Date of mailing of the international search report

06/12/2005

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Patosuo, S

INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP2005/012266

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 24, 11 May 2001 (2001-05-11) -& JP 2001 179990 A (CANON INC), 3 July 2001 (2001-07-03) cited in the application abstract paragraphs '0010! - '0012! paragraphs '0019!, '0023! - '0060! paragraphs '0075! - '0080! -----	1-9
Y	GB 2 278 845 A (* AJINOMOTO CO INC; * AJINOMOTO CO., INC) 14 December 1994 (1994-12-14) page 13, lines 3-8 -----	1-9
Y	US 2002/019500 A1 (ROTH MARTIN ET AL) 14 February 2002 (2002-02-14) paragraph '0067! -----	1-9
Y	EP 0 411 839 A (CANON KABUSHIKI KAISHA) 6 February 1991 (1991-02-06) page 11, lines 50,51 -----	1-9
A	EP 1 380 422 A (CANON KABUSHIKI KAISHA) 14 January 2004 (2004-01-14) paragraphs '0026! - '0028! paragraphs '0034! - '0049!, '0052!, '0053! paragraphs '0071! - '0092! figures 1A-2D,10-18 -----	1-9
A	US 4 004 043 A (HIRAOKA ET AL) 18 January 1977 (1977-01-18) the whole document -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/JP2005/012266

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1380425	A	14-01-2004	CN 1475350 A	18-02-2004
			JP 2004046217 A	12-02-2004
			TW 221122 B	21-09-2004
			US 2004131957 A1	08-07-2004
EP 1380423	A	14-01-2004	CN 1475352 A	18-02-2004
			JP 2004042650 A	12-02-2004
			TW 225448 B	21-12-2004
			US 2004072107 A1	15-04-2004
JP 2001179990	A	03-07-2001	NONE	
GB 2278845	A	14-12-1994	DE 4419874 A1	22-12-1994
			JP 7056336 A	03-03-1995
US 2002019500	A1	14-02-2002	NONE	
EP 0411839	A	06-02-1991	JP 3148655 A	25-06-1991
EP 1380422	A	14-01-2004	CN 1476977 A	25-02-2004
			JP 2004042389 A	12-02-2004
			TW 590898 B	11-06-2004
			US 2004070643 A1	15-04-2004
US 4004043	A	18-01-1977	CA 1044068 A1	12-12-1978
			DE 2642269 A1	31-03-1977
			FR 2325961 A1	22-04-1977
			GB 1494309 A	07-12-1977
			IT 1077027 B	27-04-1985
			JP 53043820 B	22-11-1978

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.